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The Relaxation of the Cybotactic Structure of Amorphous Solids and the Mechanism of Formation of Crystal Nuclei

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Abstract

The softening range of amorphous solids is considered to be the temperature range in which the relaxation of the cybotactic structure of the substances takes place. By applying van't Hoff's reaction-isochore to the cybotactic equilibrium in the super-cooled liquid state of glycerol, ethyl alcohol and *dl*-lactic acid, the general tendency of the contribution of the effect of cybotactic decomposition to the temperature dependence of the specific heats of these substances in this state was examined. When the number of constituent molecules of a cybotactic crystal becomes infinite, a sharp and well defined temperature is found, below which some cybotactic crystals, but above which none can exist as such. This well defined temperature is the highest at which the crystal nuclei can be formed in equilibrium; and it is designated as the melting point of the substance. Lastly, regarding the relation between the latent heats of fusion of the monoatomic elements and their melting points, a rather satisfactory explanation is proposed.

Introduction

In previous papers¹ published recently a cybotactic theory of amorphous solids and super-cooled liquids was proposed by the writer. In that theory an amorphous solid of a substance is considered to consist of free molecules of the substance and the cybotactic crystals having the size of the order of the unit cell of the crystal. The cybotactic crystals have no permanent stability. They are formed and decomposed spontaneously here and there in the liquid. The proportion in equilibrium of the total amount of the cybotactic crystals in reference to the total number of the free molecules is determined by the temperature, and it increases with decreasing temperature. When the temperature of a substance is lowered below the melting point of its crystal, without causing crystallization, it becomes super-cooled. On further cooling the substance gets increasingly viscous; and at last it attains the state of amorphous solid, which is supposed to contain a considerable amount of cybotactic crystals. The trans-

1. U. Yoshida: These Memoirs, A, **23**, 207, 233 (1941).

formation from the amorphous solid to the super-cooled liquid state or *vice versa* takes place in the softening temperature range, and this transformation is accompanied by a remarkable sudden change in various physical properties of the substance, though it is not so sharp and sudden as in the case of melting of a crystal. In the previous papers, such sudden change in various physical properties in the transformation temperature range was ascribed mostly to the decomposition of the cybotactic crystals of considerable amount by the rise of the temperature. More especially the remarkable increase in the specific heat at this temperature range was regarded as due to the heat absorbed by such decomposition of the cybotactic crystals. A sudden increase in the specific heat on heating in the softening temperature range, as is seen with boric oxide glass, has been found for many substances; and this seems to be a general property of amorphous substances. Among many amorphous substances, whose specific heats in the softening temperature range and in the super-cooled state have been measured, ethyl alcohol, glycerol and *dl*-lactic acid are worthy of mentioning; because the specific heats in their crystalline state have also been measured in the same temperature range. In the following, the contribution to the specific heat of the effect of decomposition of the cybotactic crystals on heating in the super-cooled liquid state was estimated with these three amorphous substances.

Relaxation of the Cybotactic Structure and the Specific Heat due to the Decomposition of the Cybotactic Crystals

The amorphous substance behaves almost as a solid at the temperatures below the softening range, and it acts as a liquid at the temperatures above that range. As is seen from the specific heat curves of ethyl alcohol, glycerol and *dl*-lactic acid, their specific heats in the state of amorphous solid are almost the same as those in their crystalline state. This seems to indicate that the constituent molecules in the amorphous solid are fixed in their positions just as in the crystalline state; and this is in good contrast with the liquid state, where the constituent molecules are free to change their positions. Thus the cybotactic exchange from the cybotactic crystals to the free molecules and *vice versa* must be considered to be almost, though not entirely, stopped in the amorphous solid. At the temperatures above the softening range the substance behaves as a liquid as is stated above, and noticeable time lag or hysteresis in the change of its physical properties following any temperature change takes place

only in, and extremely remarkably below, the softening range. Consequently the softening range can be regarded reasonably as the temperature range in which occurs the relaxation of the cybotactic structure of the substance, and the substance is transformed from the state of amorphous solid to that of super-cooled liquid on heating in this range. The amount of the cybotactic crystals in an amorphous substance at a temperature higher than the softening range can thus be taken nearly as the equilibrium value corresponding to that temperature; and the thermodynamic relation can be applied to it.

As to the cybotactic groups, several kinds consisting of different numbers of constituent molecules may be imagined¹. Among these, those composed of smaller number of molecules will require smaller amount of heat of decomposition, and their contribution to the specific heat variation accompanying temperature change will be of much minor degree when compared with that due to the cybotactic crystal, which is supposed to be the same as or larger than the unit cell of the crystal of the substance. Thus the effect of decomposition of cybotactic crystals only is taken into account in the following in approximately calculating the specific heat.

The spontaneous formation and decomposition of a cybotactic crystal in liquid can be considered as a sort of molecular aggregation and dissociation in liquid, and we shall apply van't Hoff's reaction-isochore to this case. Let us suppose that the number of constituent molecules in a cybotactic crystal is definite and to be denoted by ν . Then, by the decomposition of one cybotactic crystal ν free molecules are formed in the liquid. Next let x be the degree of decomposition of the cybotactic crystals, then the molecular and cybotactic concentrations in unit volume are proportional to νx and $1-x$ respectively. As to the heat of decomposition of one cybotactic crystal, which is denoted by L for 1 gram mol. of the cybotactic crystal, we shall consider it, for the present, to be approximately constant for the temperature intervals we are concerned. Thus, when the volume change accompanying the temperature variation is neglected, the cybotactic equilibrium corresponding to the temperature T expressed in absolute scale will be given by

$$\frac{(\nu x)^\nu}{1-x} = C e^{-\frac{L}{RT}} \dots\dots\dots (1)$$

1. U. Yoshida: These Memoirs, A, 23, 207 (1941).

where R is the gas constant (1.985 cal per degree), and C is also a constant independent of T . If we represent by L_0 the heat of decomposition per 1 gram of the cybotactic crystal, and by M the molecular weight of the substance; then, by putting $L = \nu ML_0$, the equation (1) becomes

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{C^{\frac{1}{\nu}}}{\nu} e^{-\frac{ML_0}{RT}} \quad \dots\dots\dots (2)$$

By differentiating equation (1) with T , we get

$$\frac{dx}{dT} = y \frac{ML_0}{RT^2} \quad \dots\dots\dots (3)$$

where y is

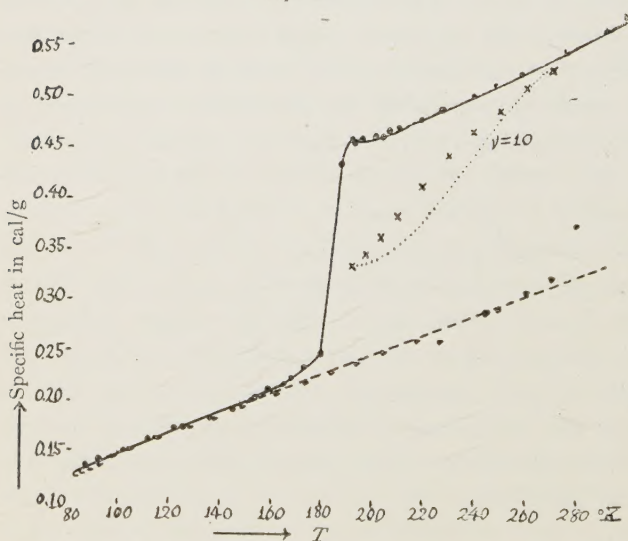
$$y \equiv \frac{\nu x(1-x)}{\nu(1-x) + x} \quad \dots\dots\dots (4)$$

The contribution C_a of decomposing the cybotactic crystals on heating, to the specific heat per 1 gram of the substance is thus

$$C_a = L_0 \frac{dx}{dT} = y \frac{ML_0^2}{RT^2} \quad \dots\dots\dots (5)$$

Now let us consider the case of glycerol as an example. The

Eig. 1
Glycerol



specific heats in amorphous and crystalline states of this substance are measured by Gibson and Giauque¹, and are shown by the curves in Fig. 1. In this figure the curve drawn in full line refers to the amorphous state and that drawn in broken line represents the value of the

specific heat in the crystalline state. The specific heat curve for the

1. G. E. Gibson and W. F. Giauque: J. Amer. Chem. Soc., **45**, 93 (1923).

crystalline state runs almost linearly with temperature, except at the temperatures just below the melting point. As this minor departure from linearity seems to be due to some experimental errors, such as caused by the presence of some impurity or in some other way, the broken line is extended straight, in the figure, up to the melting point, by considering it to represent the true value. The values of the specific heat given in Fig. 1 refer to 1 gram of the substance.

The specific heat of a substance in its super-cooled liquid state may be considered to consist of three parts: 1) The specific heat C_e of the cybotactic crystals, which may be taken to be approximately the same as that of the adult crystals at the same temperature. 2) The specific heat C_f of the free molecules which is supposed to be larger than C_e as will be imagined from the value at the melting point of the adult crystals, where almost all the molecules are likely to be in free state and not in the state of cybotactic configuration. 3) The heat C_d required for decomposition of the cybotactic crystals in raising the temperature. The temperature dependence of C_f is not obvious. However, as almost all the molecules are likely to be in the free state at the melting point of the adult crystals as is stated above, the specific heat observed for the liquid at this temperature may be taken to be approximately that of free molecules. Thus, though it may be rough, the writer assumes that the ratio C_f/C_e remains the same for all temperatures above the softening range, and is equal to that of the liquid and the adult crystals at the melting point of the latter; and the value of C_f at any temperature was calculated from the value of the specific heat of the adult crystals at the same temperature, which is considered to be approximately the same as C_e .

As to the sudden increase of the specific heat in the softening range, the writer regards it as the cybotactic relaxation. As such cybotactic relaxation is primarily caused by the increased kinetic energy of the molecules due to thermal agitation, the cybotactic exchange between free molecules and the cybotactic crystals should be noticeable in the softening range; and consequently the temperature T_2 at which the rate of the cybotactic decomposition on heating is maximum should be located somewhere about the softening range. Under such a consideration the writer designates the temperature just above the softening range as T_2 at which the maximum rate of the cybotactic decomposition takes place on heating; and in the case of glycerol T_2 is found to be at 192°K. The temperature T_2 obtained by

differentiating C_d given by equation (5) with temperature and by putting it equal to zero, is

$$T_2 = \frac{\nu^2(1-x)^2 - \nu x^2}{\{x + \nu(1-x)\}^2} \frac{ML_0}{2R} = Y \frac{ML_0}{2R} \dots\dots\dots(6)$$

where

$$Y \equiv \frac{\nu^2(1-x)^2 - \nu x^2}{\{x + \nu(1-x)\}^2} \dots\dots\dots(7)$$

The value of x in (6) is not independent, and if we put $T = T_2$ in the equation (2) and eliminate x from equations (2) and (6), we get the relation between T_2 and ML_0 . Consequently the equation (6) must be regarded as the equation showing the relation between T_2 and ML_0 . The degree of decomposition x_2 at the temperature T_2 is obtained by putting $T = T_2$ in equation (2), as follows:

$$\frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} = \frac{C^{\frac{1}{\nu}}}{\nu} e^{-\frac{ML_0}{RT_2}} \dots\dots\dots(8)$$

From equations (2) and (8), the relation between the degree of cybotactic decomposition x and the temperature T thus becomes

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} e^{-\frac{ML_0}{R} \left(\frac{1}{T} - \frac{1}{T_2} \right)} \dots\dots\dots(9)$$

By denoting the values of C_d , y and Y at the temperature T_2 by $C_{d,2}$, y_2 and Y_2 respectively, we obtain from equations (5) and (6)

$$C_{d,2} = y_2 \frac{ML_0^2}{RT_2^2} \dots\dots\dots(10)$$

and

$$T_2 = Y_2 \frac{ML_0}{2R} \dots\dots\dots(11)$$

By eliminating L_0 from equations (10) and (11), we get

$$\frac{Y_2^2}{y_2} = \frac{4R}{C_{d,2}M} \dots\dots\dots(12)$$

Thus if we know the value of $C_{d,2}$, the value of $\frac{Y_2^2}{y_2}$ is obtained; and consequently the value of x_2 can be obtained for a given number of ν . As to the value of ν , the number of the constituent molecules for one cybotactic crystal, we do not know any thing definitely. But if we consider the cybotactic crystal to be the same as or greater than the unit cell of the crystal of the substance, then ν must be the same as or greater than the number of constituent molecules of the unit-cell of the crystal. Thus the writer have assigned the values of

5, 10, 15, 20, 30, $\frac{x}{(1-x)^{\frac{1}{\nu}}}$
50, 100 etc. to ν ; and investigated the temperature dependence of C_a , to understand rather qualitatively the temperature change of the specific heat of the super-cooled liquid at the temperatures higher than the softening range. For numerical calculation the writer has plotted the curves showing the values of $\frac{x}{(1-x)^{\frac{1}{\nu}}}$, y , Y and $\frac{Y^2}{y}$ for

Fig. 2.

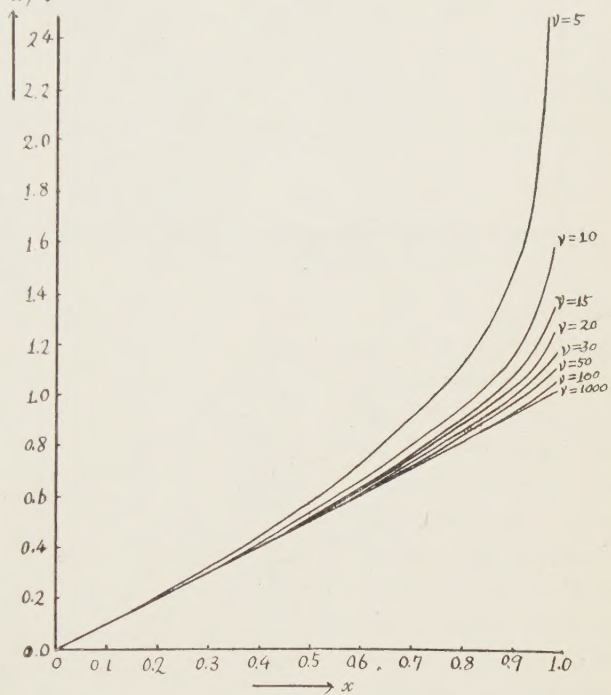
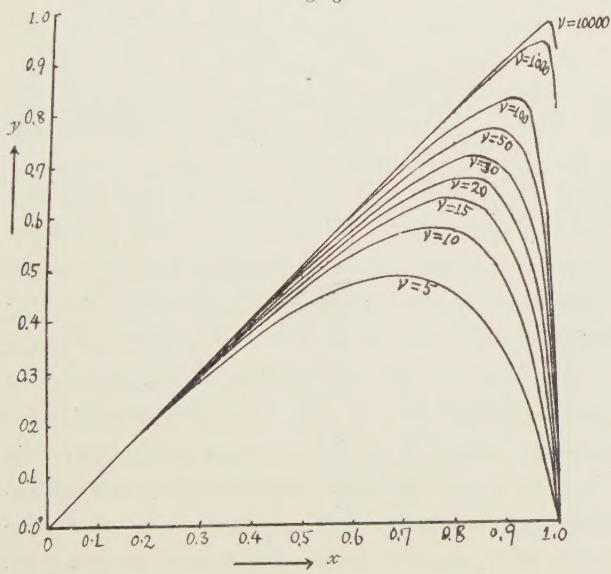


Fig. 3



various values of x by assigning the numbers stated above to ν . These curves are shown in Figs. 2, 3, 4, and 5.

As stated above the writer assumes that the ratio C_f/C_e of the specific heats of the free molecules and that of the cybotactic crystals in the state of super-cooled liquid is the same for dif-

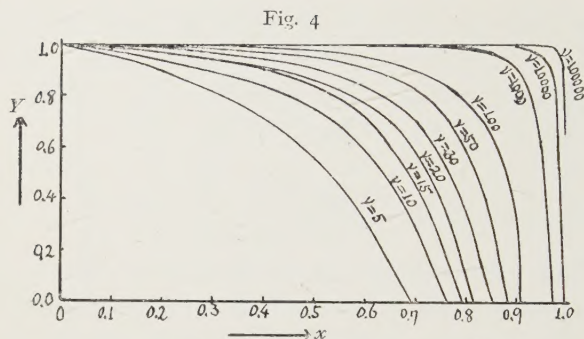


Fig. 4

ferent temperatures, and takes the value of the ratio of the specific heat of the liquid and that of the adult crystal of the same substance at the melting point of the latter; and he also assumes that the spe-

cific heat of the cybotactic crystals at any temperature is the same as that of the adult crystal at the same temperature. By this assumption the values of C_f and C_c at the temperature T_2 , where the rate of decomposition of the cybotactic crystals is supposed to be maximum, and at the temperatures higher than T_2 , are obtained immediately. Next

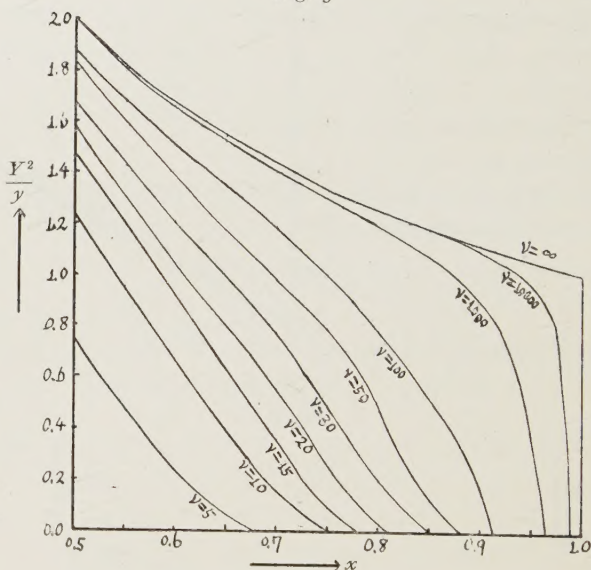


Fig. 5

we must know the values of L_0 and x_2 . The specific heat of the amorphous substance at the temperature T_2 consists of $x_2 C_f$, $(1-x_2)C_c$ and $C_{a,2}$. Thus if we give a certain value arbitrarily to x_2 , we obtain $x_2 C_f + (1-x_2)C_c$; and consequently the value of $C_{a,2}$ is obtained immediately by subtracting the value of $x_2 C_f + (1-x_2)C_c$ from the observed value of the specific heat of the amorphous substance at the temperature T_2 . By putting this value of $C_{a,2}$ into the equation (12) we get graphically again the value of x_2 for a given value of ν . As this value of x_2 must be the same as that initially taken arbitrarily, the method of successive approximation was adopted to get the coincidence. Coincident value of x_2 having been obtained in such a way,

we can find the value of L_0 from either one of the equations (10) and (11) for the same value of ν as before. As for a given value of Y_2^2/y_2 the value of x_2 is different for different values of ν ; consistent values $C_{d,2}$, x_2 and L_0 are also different for various values of ν as is shown in Table I for glycerol. The values of ML_0Y_2/T_2 given in the last column of the table are calculated with the values of L_0 and Y_2

Table I
Glycerol
 $M=92$, $T_2=192^\circ K$, T_m (melting point) $=292^\circ K$, heat of fusion 47.5 cal/g

ν	x_2	L_0	ML_0	Y_2	$C_{d,2}$	$\frac{ML_0}{T_2}$	$\frac{ML_0}{T_2} Y_2$
5	0.514	15.6	1437	0.525	0.130	7.47	3.92
10	0.59	13.7	1260	0.610	0.121	6.56	4.00
20	0.657	12.4	1140	0.670	0.114	5.94	3.98
30	0.685	11.3	1043	0.730	0.103	5.44	3.97
50	0.72	10.5	966	0.785	0.097	5.03	3.95
100	0.76	9.86	907	0.840	0.090	4.73	3.97
1000	0.84	8.63	794	0.960	0.078	4.13	3.97
10000	0.86	8.30	764	0.998	0.074	3.98	3.97

which are tabulated in the table. As is seen with equation (11), the value of ML_0Y_2/T_2 should be equal to $2R=3.97$, irrespective of the value of ν ; and this requirement is seen to be satisfied from the table.

With the values of x_2 and L_0 as are given in Table I, the degree x of decomposition for various values of T is calculated with equation (9) for several assigned values of ν ; and the specific heat C_d due to the decomposition of the cybotactic crystals by the rise of temperature is obtained with equation (5). The temperature dependence of x and C_d thus obtained for various values of ν are shown

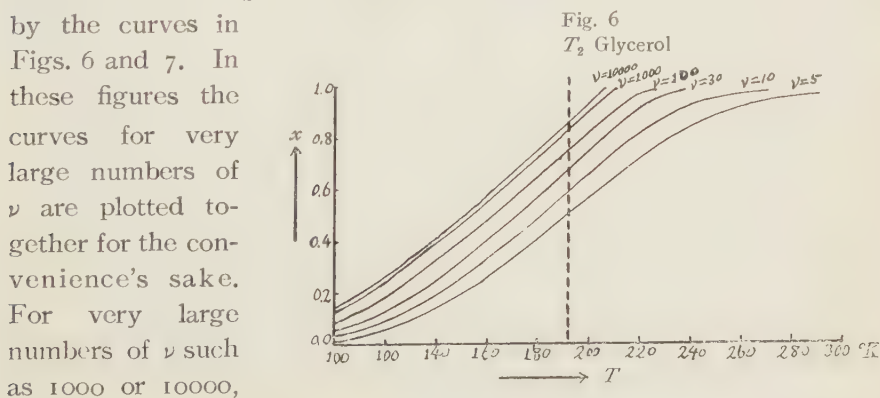
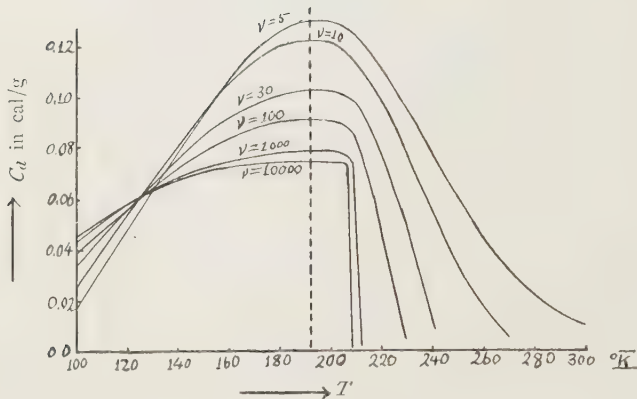


Fig. 7
 T_2 Glycerol



the curves have very sharp break at the last stage of the cybotactic decomposition. This seems to correspond to the upper limit of the temperature for the existence of the crystal nuclei; and this point

will be considered later.

As to the number of the constituent molecules of a cybotactic crystal, the writer considers it to be roughly of the order of those contained in a unit cell of the crystal of the substance; but no definite value is known. However, in order to understand the general tendency of the contribution of the cybotactic decomposition to the specific heat of the super-cooled liquid, the calculation was carried out for several different values of ν taken arbitrarily, so as to be consistent with the observed value of the specific heat at the T_2 point. The results are given in Table I and in Figs. 6 and 7. At the T_2 point, which was taken as 192°K for glycerol, the value of $C_{a,2} + x_2 C_f + (1-x_2) C_e$ was taken as the same with the observed value of the specific heat in the amorphous or super-cooled liquid state at that temperature. The fact that the values of x_2 , $C_{a,2}$ and L_0 differ with ν , as is seen in Table I, is due to these circumstances; and it does not signify that these values change in such a manner as is shown in the table by the actual increase of the number of the constituent molecules of a cybotactic crystal accompanying to its growth.

In Figs. 6 and 7 the values of x and C_d calculated even at the temperatures below the T_2 point are plotted. But the curves below this point have no significance other than the theoretical one. In the softening temperature range just below the T_2 point the cybotactic structure of the substance tightens or relaxes almost exactly as it is according as it is cooled or heated. At the temperatures below this range any noticeable cybotactic exchange in approaching to the idealised equilibrium state is considered to be almost arrested. However,

by passing the T_2 point on heating the cybotactic exchange begins to be very active, and the equilibrium is likely to be almost attained at the temperatures higher than this point. Under this consideration, the calculated values of C_d only for the temperatures higher than T_2 are represented in Fig. 1, by the curve drawn in dotted line, for $\nu=10$, by subtracting the value of C_d respectively from those of the specific heat observed in the super-cooled state. As to the definite number of the constituent molecules of a cybotactic crystal we are entirely ignorant as is stated above, but the number 10 was chosen in Fig. 1 as of a reasonable order, so that we may understand the general tendency of the contribution of the cybotactic decomposition to the specific heat of the super-cooled liquid.

The contribution of the presence of the cybotactic crystals and the free liquid molecules to the specific heat of the super-cooled glycerol, i. e. $x C_f + (1-x) C_e$, was calculated. As is stated above the writer assumes that the specific heat C_e of the cybotactic crystals is the same as that of the adult crystal at the same temperature, and that the ratio C_f/c_e remains the same for all temperatures, and he takes the value of the ratio of the specific heats of the liquid and of the adult crystal at the melting point of the latter. Under this assumption the values of $x C_f + (1-x) C_e$ are readily obtained for all temperatures from the values of x already calculated, and they are represented by the crosses in Fig. 1. The position of the crosses does not coincide exactly with the curve drawn in dotted line in Fig. 1. But if we consider that the calculation is made on very rough approximation by assuming the proportionality of C_f/C_e and by disregarding the temperature variation of the latent heat of fusion of the cybotactic crystals, a small discrepancy such as seen in Fig. 1 may be overlooked.

Specific heat measurement both in amorphous and crystalline states of the same substance was also made with ethyl alcohol¹ and *dl*-lactic acid². With these two substances the writer carried out the same calculation as with glycerol, and obtained entirely similar results as with it. Important numerical data for the case of $\nu=10$ are given in Table II, and the results of calculation are shown in Figs. 8 and 9 entirely in the same manner as with glycerol. After all, an enor-

1. G. S. Parks: J. Amer. Chem. Soc., **47**, 338 (1925); K. K. Kelley: J. Amer. Chem. Soc., **51**, 779 (1929).

2. S. Parks, S. B. Thomas and D. W. Light: J. Chem. Phys. **4**, 64 (1936).

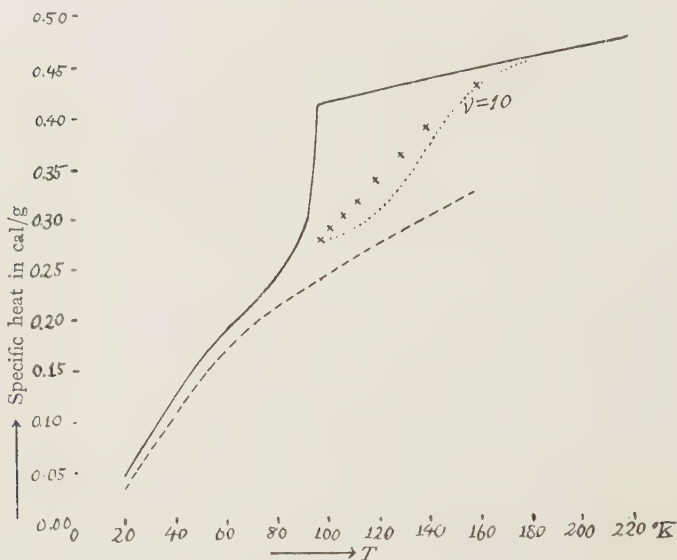
Table II

	M	T_m in $^{\circ}K$ (melting point)	T_2 in $^{\circ}K$	ν	x_2	L_0 cal/g
Ethyl alcohol	46	159	98	10	0.495	11.25
<i>dl</i> -lactic acid	90	290	211	10	0.60	15.7
Glycerol	92	292	192	10	0.59	13.7

mous increase of the specific heat of an amorphous substance above the softening temperature range is partly ascribed to the decomposition of the

cybotactic crystals, and thus a part of the sudden increase in the specific heat at the T_2 point is accounted for by this fact. As to the remaining part of this sudden increase the writer considers it, as is stated above, to be due to the relaxation of the cybotactic structure

Fig. 8
Ethyl alcohol

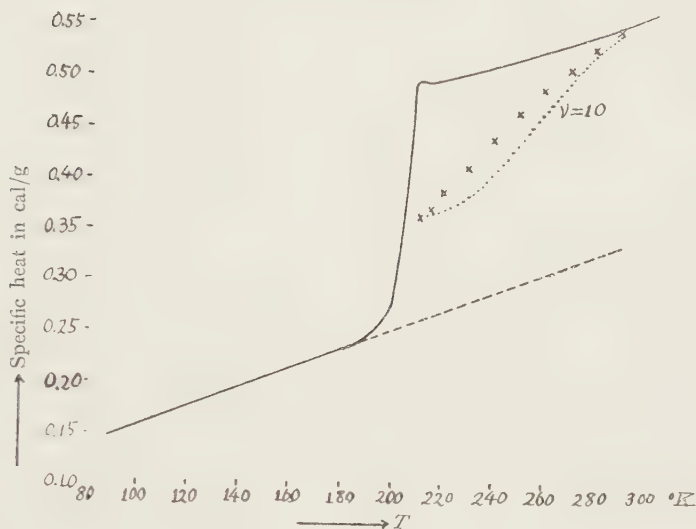


in the softening range, by making the free molecules and the cybotactic crystals behave freely just as in ordinary liquid.

Among many physical properties of amorphous substances which change abruptly in the softening range, the viscosity seems to be especially worthy of mentioning. With many substances their viscosity in the viscous liquid state above the softening range of temperature has been studied¹. Extrapolation of measurement into the softening

1. Parks, Barton, Spaght and Richardson: *Physics*, **5**, 193 (1934); Parks and Gilkey: *J. Phys. Chem.*, **33**, 1428 (1929).

Fig. 9
*d**l*-Lactic acid



range shows that, at the middle point of the softening range, the viscosity of the substances is of the same order and takes the value lying between 10^{13} and 10^{14} poises. This rule appears to hold irrespective of the kind of the substance or of the mean temperature at which the softening takes place, as was pointed out by J. D. Ferry and G. S. Parks¹. According to the writer this is mainly due to the presence of almost the same cybotactic composition in the softening range for different amorphous substances. In the case of ethyl alcohol, *d**l*-lactic acid and glycerol the values of x_2 at the T_2 point lie between 0.5 and 0.6; and it seems not unnatural to consider that the degree of cybotactic decomposition in the softening range is of the order of these figures for all amorphous substances.

In previous papers² the writer has proposed a cybotactic theory of the amorphous Beilby layer, which is supposed to exist on a polished metal surface and in very narrow interstices between neighbouring crystals of metals; and the phenomenon of recrystallization of metals is ascribed primarily to the melting of the amorphous layer between neighbouring crystals and to the growth of the crystal nuclei formed spontaneously in the melt. If the writer's view of the

1. J. Chem. Phys., **4**, 70 (1936).

2. U. Yoshida: These Memoirs, A, **23**, 207, 233, 325, 351 (1941).

cybotactic structure of the Beilby layer is admitted, the melting of the Beilby layer means the same thing as the relaxation of the cybotactic structure of an amorphous substance in its softening temperature range, and the lowest recrystallization temperature of a metal comes to signify the T_2 point just above the softening temperature range of Beilby's amorphous layer of the metal.

Formation of the Crystal Nuclei in the Melt, and the Relation between the Latent Heat of Fusion and the Melting Point of Adult Crystals

The melting point of the adult crystal of a substance is entirely fixed, and its two phases as liquid and crystal can coexist only at its melting point. This point was explained, in a former paper, by considering the phenomena of melting and crystallization of a substance as a surface phenomenon taking place at the boundary surface of the crystal and the melt. The same point seems to be also explained from the view point of the cybotactic equilibrium by taking the number of constituent molecules of a cybotactic crystal as infinite. As is stated in the case of the cybotactic equilibrium of glycerol the C_a curve i. e. the $\frac{dx}{dT}$ curve for a very great number of ν has a very sharp break at the last stage of the cybotactic decomposition. This property of the $\frac{dx}{dT}$ curve is not confined to any particular kind of substance, but it is universal. We shall apply this property of the $\frac{dx}{dT}$ curve to the formation of the crystal nuclei in any kind of liquid in general. When the number ν of constituent molecules of a cybotactic crystal becomes infinite we can regard it as a crystal nucleus or even as an adult crystal when sufficiently great. Thus the temperature at which the value of x becomes 1 and that of $\frac{dx}{dT}$ drops suddenly to zero is the limiting temperature, below which the very small crystals or the crystal nuclei can, and above which can not, exist as such in equilibrium. Below the limiting temperature, if some of the very small crystal nuclei, though small in their number, have grown by chance to a considerable size, they will now become endowed with sufficient stability, and their further growth up to the adult crystals will take place thoroughly by the surface phenomenon as in the case of the growth of the adult crystals. Considered in such a way, the limiting temperature at which the value of $\frac{dx}{dT}$ falls suddenly to zero at the

final stage of cybotactic decomposition, is nothing but the melting point of the substance. Below this temperature, the degree x of decomposition of the crystal nuclei should decrease with decreasing temperature according to the present theory: i. e. the number of crystal nuclei should increase with decreasing temperature. This is in good accord with the observations of Tammann and others¹.

As the value of $\frac{dx}{dT}$ falls abruptly at the melting point T_m , this point will be obtained from equation (3) by differentiating it with T , and by finding the point at which the value of $\frac{d^2x}{dT^2}$ suddenly becomes $-\infty$. So we get from equation (3)

$$\frac{d^2x}{dT^2} = \frac{ML_0}{RT^3} \gamma \left\{ \frac{ML_0}{RT} Y - 2 \right\} \dots \dots \dots (13)$$

where γ and Y represent

$$\gamma = \frac{\nu x(1-x)}{x + \nu(1-x)}, \quad Y = \frac{\nu^2(1-x)^2 - \nu x^2}{\{x + \nu(1-x)\}^2} \dots \dots \dots (14)$$

When ν is sufficiently great, the values of γ and Y tend to become x and 1 respectively, except at $x=1$. Moreover, when x tends to become 1 the value of Y turns to $-\infty$ abruptly from its initial value of 1 by passing through the zero value. Consequently the point at which the value of $\frac{d^2x}{dT^2}$ abruptly turns to $-\infty$ can be designated by putting

$$\nu^2(1-x)^2 - \nu x^2 = 0, \\ \text{i. e.} \quad 1-x = \frac{x}{\nu^{\frac{1}{2}}} \dots \dots \dots (15)$$

for very large value of ν , and this is the condition to get the melting point definitely. Next the relation between the melting point T_m and the T_2 point is obtained by putting this condition into equation (9).

As
$$\lim_{\nu \rightarrow \infty} \frac{(1-x)^{\frac{1}{\nu}}}{x} = \lim_{\nu \rightarrow \infty} \frac{x^{\frac{1}{\nu}}}{x \nu^{\frac{1}{2\nu}}} = 1,$$

and
$$\lim_{\nu \rightarrow \infty} (1-x_2)^{\frac{1}{\nu}} = 1,$$

we get from equation (9), at $\nu \rightarrow \infty$,

$$\frac{1}{x_2} = e^{-\frac{ML_0}{R} \left(\frac{1}{T_m} - \frac{1}{T_2} \right)} \dots \dots \dots (16)$$

Thus the temperature difference between the melting point T_m and

1. G. Tammann: Kristallisieren u. Schmelzen, p. 151 (1903).

the T_2 point is determined by the degree x_2 of cybotactic decomposition at the T_2 point. When x_2 is nearly equal to 1 T_m approaches to T_2 , and when it becomes less T_m becomes higher.

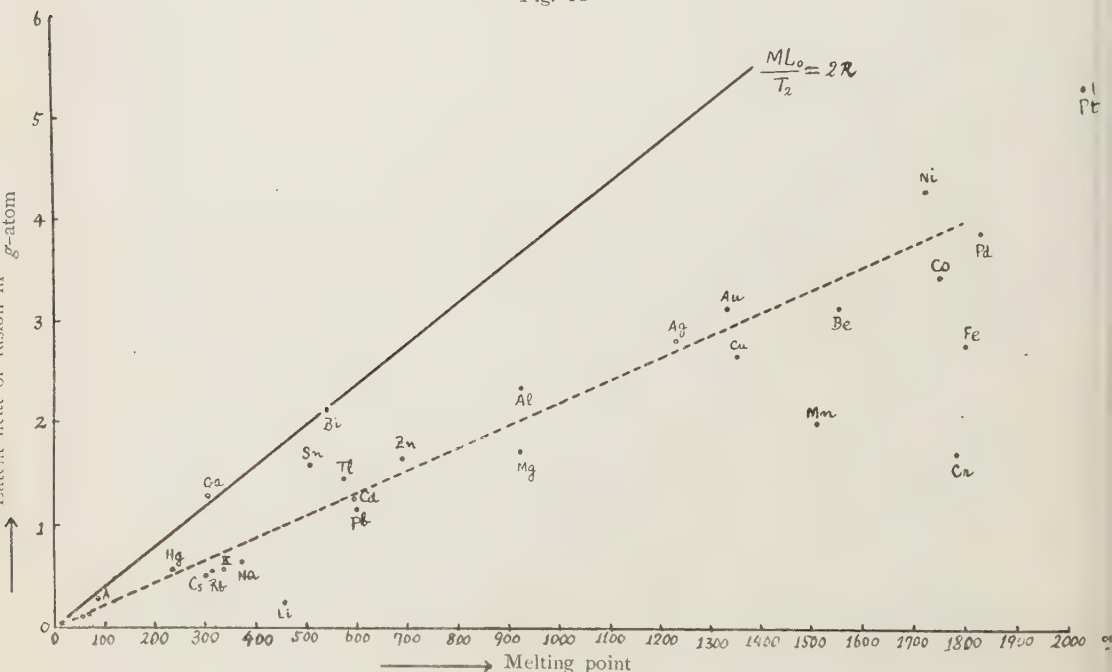
When the T_2 point takes place at a value of x_2 which is definitely smaller than 1, the value of Y tends to 1 for very large value of ν ; and the T_2 point obtained by equating the right hand side of equation (13) to zero becomes in this case

$$\frac{ML_0}{T_2} = 2R \dots \dots \dots (17)$$

As the value of x_2 is definitely smaller than 1 in this case, the melting point T_m must be certainly higher than T_2 as is seen from equation (16). As to the value of ML_0 it is considered by the writer that it increases with the value of ν and approaches to the value of the adult crystal asymptotically. Thus if we assume that the value of ML_0 of the crystal nuclei is almost the same as that of the adult crystal of the same substance, the relation between ML_0 and T_m comes to be expressed by

$$\frac{ML_0}{T_m} < 2R \dots \dots \dots (18)$$

Fig. 10



This inequality shown in the relation between the latent heat of fusion and the melting point is satisfied actually by the monoatomic elements except gallium as is shown by Fig. 10. In this figure, the observed values of latent heat of fusion of various monoatomic elements which are expressed in Kilo-calorie per g-atom, are plotted as ordinates against the melting points taken as abscissae. Here most of the observed values of latent heat of fusion are taken from International Critical Table, and a few others from Landolt-Börnstein's Physikalisch-Chemische Tabellen. In the figure the relation $ML_0/T_2 = 2R$ is represented by the straight line drawn in full, and for the monoatomic elements except gallium the values of ML_0/T_m take the positions beneath this straight line as is expected from the inequality (18). However, when the T_2 point takes place at a value of x_2 which is almost equal to 1 for a very large number of ν , the circumstances are different. In this case T_m approaches very close to T_2 , as will be seen from equation (16); and the value of Y becomes somewhat smaller than 1 even for a very large number of ν , as will be seen from Fig. 4. Thus from the condition to cause the T_2 point, which is obtained by equating the right hand side of equation (13) to zero, we get

$$\frac{ML_0}{RT_2} > 2 ;$$

and by replacing T_2 by T_m , by the reason stated above, it becomes

$$\frac{ML_0}{T_m} > 2R \dots\dots\dots (19)$$

This shows that ML_0/T_m can take the value greater than $2R$ in some exceptional case, as is actually so with Ga, which occupies the position somewhat greater than $2R$ in its value of ML_0/T_m in Fig. 10.

The reason why the degree x_2 of decomposition at the T_2 point is different for different substances is not entirely clear to the writer. But this can be interpreted to some extent in the other way by the difference of the value of ML_0/T_2 . By rewriting equation (11), we get

$$Y_2 = - \frac{2R}{\frac{ML_0}{T_2}} \dots\dots\dots (20)$$

As is stated above the value of ML_0/T_2 is equal to $2R$ for the majority of the monoatomic elements, and Y_2 takes the value of 1 in this case. The value of x_2 corresponding to this value of Y_2 for a very great number of ν is, of course, smaller than 1; but, as is seen from

Fig. 4, it is rather indeterminate and may take a much smaller value, as is actually so for the majority of the monoatomic elements. When the value of ML_0/T_2 is greater than $2R$, Y_2 becomes smaller than 1; and this occurs at a value of x_2 very near to 1, as is stated above for gallium.

It is worth while to note that common metals, most of which take the crystal form of face-centred cubic or of hexagonal closed packed, are crowded near the straight line drawn broken in Fig. 10. The writer calculated, by making $(ML_0)/(RT_2)=2$, the value of x_2 with equation (16) from the inclination of this straight line, and found it to be $x_2=0.41$. This is much smaller than 1, and furnishes the reason for the fact that these metals are situated much lower than the critical position represented by $ML_0/T_m=2R$.

In the above consideration the writer has disregarded the variation of the latent heat of fusion with temperature, which arises from the difference of the specific heats in liquid and crystalline phases of the same substance. But, considered from the results of measurements made on several kinds of elements, such difference of the specific heats in the two different phases seems generally to be not noticeable in the case of the elements; and the good agreement between theory and observation as was stated above seems to have arisen from this fact.

With inorganic compounds, and more especially with organic compounds, the values of $(ML_0)/(T_m)$ are generally much larger than the critical value $(ML_0)/(T_m)=2R$. At the same time the specific heats in liquid and in crystalline phases are remarkably different in general, being greater in liquid, as will be seen for example in Figs. 1, 8 and 9 with glycerol, ethyl alcohol and *d/l*-lactic acid respectively. In such cases the latent heat of fusion will change considerably with temperature, and the above consideration on the relationship between the latent heat of fusion and the melting point becomes inapplicable. With complex molecules of inorganic compounds, and more especially of organic compounds, some excess energy is required in setting up some more degree of freedom of molecular motion by melting, in addition to that necessary to decompose the constituent molecules from the lattice points of the crystal. If this reasoning is correct, the calculations made before by the cybotactic decomposition of glycerol, ethyl alcohol and *d/l*-lactic acid are not perfect; and they must be looked upon as showing rather qualitatively the general tendency of the con-

tribution of the cybotactic decomposition to the temperature dependence of the specific heats of these substances in their super-cooled state.

Lastly it must be noted that the writer found, during the course of the proof reading that the monoatomic elements Ne, Kr, Xe and Rn take the positions in Fig. 10 just beneath the straight line $ML_0/T_2 = 2R$, in good accord with the present theory.

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Condition nécessaire et suffisante remplie par les Équations différentielles ordinaires sans points de Peano

par Hirosi Okamura

(Reçu le 3 Juin, 1941)

Il est bien connu, depuis Peano, qu'il existe une solution (au moins) issue d'un point initial donné, pour un système normal d'équations différentielles ordinaires avec seconds membres continus, et que certaines conditions imposées aux équations, par exemple, celle de Lipschitz, sont suffisantes pour qu'un système différentiel ne possède qu'une seule solution passant par un point quelconque du domaine de définition, ou en d'autres termes, que le système soit dépourvu de points de Peano, c'est-à-dire points d'embranchement des courbes solutions du système. Quelle est, alors, la condition nécessaire et, en même temps, suffisante pour que se trouve une telle circonstance d'unicité? C'est à cette question que nous allons donner une réponse dans le présent Mémoire.

Beaucoup d'études ont été faites concernant l'unicité des solutions des équations différentielles, mais elles tiennent, presque toutes, à des conditions seulement suffisantes de l'unicité, tandis que nous savons déjà quelques conditions nécessaires et suffisantes de l'unicité en un point initial donné¹; d'ailleurs, ces conditions se rattachent, soit explicitement ou non, à une solution particulière issue du point initial considéré, et quelques-unes d'elles ne sont valables qu'au cas d'une équation unique. Pourtant, il s'agit ici, comme condition nécessaire et suffisante de l'unicité réalisée partout dans un voisinage d'un point du domaine,² d'une ou deux inégalités où interviennent seulement les équations et non pas leurs solutions; ce que personne n'a établi jusqu'aujourd'hui.

La condition obtenue est presque celle que nous avons donnée autrefois, comme condition suffisante de l'unicité pour une équation

1. Yosie, Jap. J. Math. **2** (1925), p. 161; Okamura, ces Memoirs A **17** (1934), p. 319 [Correction, A **19** (1936), p. 269], ibid. A **23** (1941), p. 225.

2. Il y a là une difficulté pour établir un pareil résultat pour le domaine entier et nous nous bornerons, dans ce Mémoire, au point de vue local.

unique¹, et la démonstration ne s'effectue que d'après la méthode que nous avons introduite récemment², complétée par quelque artifice d'une certaine moyenne intégrale.³

Ainsi, nous sommes à établir la proposition suivante :

Théorème.—*Considérons un système différentiel réel*

$$\frac{dy_i}{dx} = F_i(x, y_1, \dots, y_n) \quad (i=1, 2, \dots, n)$$

où F_i sont fonctions continues dans un domaine C de points $(x, y_1, \dots, y_n)$; et supposons que ce système n'admet qu'une seule courbe solution issue à droite d'un point initial quelconque, intérieur de C . Alors, si nous prenons un domaine⁴

$$V: a < x < a', \quad b_i < y_i < b'_i \quad (i=1, \dots, n)$$

qui se trouve, ainsi que sa frontière, dans l'intérieur de C , il existe une fonction $\Phi(x, y_1, \dots, y_n, z_1, \dots, z_n)$ définie pour

$$W: a < x < a', \quad b_i < y_i < b'_i, \quad b_i < z_i < b'_i \quad (i=1, \dots, n),$$

continue, ainsi que ses dérivées partielles du premier ordre, par rapport à ces $2n+1$ variables $(x, y_1, \dots, y_n)$ dans W , et telle que

$\Phi(x, y_1, \dots, y_n) > 0$ ou $= 0$ selon que $|y_1 - z_1| + \dots + |y_n - z_n| > 0$ ou $= 0$, et

$$\begin{aligned} \frac{\partial \Phi(x, y_1, \dots, y_n)}{\partial x} + \sum_{i=1}^n \frac{\partial \Phi(x, y_1, \dots, y_n)}{\partial y_i} F_i(x, y_1, \dots, y_n) \\ + \sum_{i=1}^n \frac{\partial \Phi(x, y_1, \dots, y_n)}{\partial z_i} F_i(x, z_1, \dots, z_n) \leq 0. \end{aligned}$$

La réciproque est évidente : sous ces conditions, il n'existe qu'une seule courbe solution issue à droite d'un point donné mais arbitraire de V .⁵

On a un résultat analogue pour l'unicité à gauche, en renversant cette fois, seulement, le sens de la dernière inégalité ci-dessus. Par conséquent, en combinant ces résultats, on aura une condition nécessaire et suffisante pour l'unicité à droite et à gauche dans un voisinage d'un point donné ; la condition exige l'existence de deux fonctions, telles que nous venons d'indiquer.

1. Loc. cit. (1934), p. 322, Corollaire.

2. Loc. cit. (1941).

3. MM. Kakeya et Tsuji ont utilisé cet artifice dans leurs recherches relatives aux équations différentielles ordinaires [Jap. J. Math. **16** (1939), p. 71].

4. On pourrait prendre un domaine plus général sans changement essentiel de nos raisonnements, mais nous n'insisterons pas sur ce point peu important pour le problème local où nous nous plaçons.

5. Parce que, pour deux solutions $y_i = y_i(x)$, $z_i = z_i(x)$, la fonction $\Phi[x, y_1(x), \dots, z_n(x)]$ n'est pas croissante par rapport à x , étant égale à 0 pour x initial, donc elle doit être identiquement nulle, d'où les identités $y_i(x) = z_i(x)$ ($i=1, \dots, n$).

Nous allons démontrer ce Théorème, et après cela nous en ajouterons quelques exemples particuliers.

I.—Démonstration du Théorème.

1. Nous nous bornerons, pour plus de clarté, au cas $n=1$ (y, z, b, b' au lieu de y_1, z_1, b_1, b'_1) et laissons de côté le cas général qui est tout à fait analogue à ce cas simple.

Considérons alors les équations simultanées

$$(F) \quad \frac{dy}{dx} = F(x, y), \quad \frac{dz}{dx} = F(x, z),$$

qui n'admet, d'après hypothèse, qu'une courbe solution issue à droite d'un point du domaine de définition, et, en particulier, une seule courbe située, jusqu'au bout, sur le plan $y=z$, partant à droite d'un point de ce plan.

Prenons un domaine fermé

$$V_1: a-\varepsilon \leq x \leq a'+\varepsilon, \quad b-\varepsilon \leq y \leq b'+\varepsilon$$

avec ε positif mais assez petit, tel que V_1 est contenu, avec sa frontière, dans l'intérieur de C , contenant V dans son intérieur, et prenons aussi un domaine fermé

$$W_1: a-\varepsilon \leq x \leq a'+\varepsilon, \quad b-\varepsilon \leq y \leq b'+\varepsilon, \quad b-\varepsilon \leq z \leq b'+\varepsilon.$$

Cela étant, construisons, suivant les définitions que nous avons données récemment¹, la fonction $D(P, Q)$ pour le système (F) et pour le domaine W_1 , P et Q étant deux points quelconques de W_1 . Cette fonction $D(P, Q)$ jouit, comme nous avons indiqué¹, des trois propriétés suivantes: 1° $D(P, Q)$ est une fonction finie et continue de deux points quelconques P et Q de W_1 et s'annule si et seulement si P et Q se trouvent sur une même courbe solution de (F), courbe située dans W_1 (frontière comprise), sinon $D(P, Q) > 0$; 2° $D(P, Q)$ est une fonction décroissante de l'abscisse (x) de Q , lorsqu'on fait varier le point Q sur une même courbe solution de (F), restant à droite de P ; 3° $D(P, Q)$ satisfait à la condition de Lipschitz

$|D(P, Q) - D(P, Q')| \leq \overline{QQ'}$ pour Q et Q' d'une même abscisse (x), $\overline{QQ'}$ désignant la longueur du segment QQ' .

2. Nous introduisons ensuite une fonction $\delta(Q)$, Q étant un point arbitraire de W_1 , telle que $\delta(Q)$ soit le minimum de $D(P, Q)$ pour toutes les positions du point P pris sur le plan $y=z$, ayant son abscisse (x) inférieure ou égale à celle de Q , c'est-à-dire, P étant à gauche de Q . Alors, par la nature des fonctions continues, il existe un point P de W_1 , sur le plan $y=z$ et à gauche de Q , tel que

1. Loc. cit. (1941). § II.

$D(P, Q) = \delta(Q)$; donc, d'après hypothèse et d'après la propriété de $D(P, Q)$ (1°, n° 1), $\delta(Q)$ s'annule si et seulement si le point Q vient sur le plan $y=z$, sinon $\delta(Q) > 0$. De plus, $\delta(Q)$ est une fonction continue de Q , décroissante par rapport à l'abscisse (x) de Q lorsque Q se meut sur une même courbe solution de (F), et enfin, elle vérifie la condition de Lipschitz

$$|\delta(Q) - \delta(Q')| \leq \overline{QQ'} \text{ pour deux points } Q \text{ et } Q' \text{ de même abscisse } (x).$$

Par conséquent, si nous posons

$$\varphi(x, y, z) = \delta(Q), \quad Q: (x, y, z),$$

la fonction $\varphi(x, y, z)$ est, à peu près, ce que nous cherchons et il nous reste à la substituer par une autre $\Phi(x, y, z)$, douée des dérivées continues, conservant les propriétés essentielles de φ .

3. À cet effet, posons

$$\psi(x, y, z) = e^{-r} \varphi(x, y, z),$$

et puis

$$\chi(x, y, z) = \frac{1}{(2\rho)^3} \int_{x-\rho}^{x+\rho} d\xi \int_{y-\rho}^{y+\rho} d\eta \int_{z-\rho}^{z+\rho} \psi(\xi, \eta, \zeta) d\zeta$$

pour tous points (x, y, z) de W tels que $y \neq z$, où ρ est une fonction positive de $|y-z|$:

$$\rho = \rho(r) > 0 \quad \text{pour } r = |y-z| > 0,$$

que nous préciserons, de plus en plus, dans la suite.

Supposons d'abord que

$$\rho(r) < \varepsilon \quad (0 < r < \infty);$$

donc la fonction $\chi(x, y, z)$ est bien définie dans W sauf sur le plan $y=z$.

Nous supposons ensuite que $\rho(r)$ est une fonction continue, ainsi que sa dérivée $\rho'(r)$, pour $0 < r < \infty$. Par conséquent, la fonction $\chi(x, y, z)$ possède toutes ses dérivées partielles du premier order continues, pour $y \neq z$, dans W .

Faisons hypothèse que $\rho(r)$ tende vers 0 avec r , de sorte que $\chi(x, y, z)$ est continue dans W , ayant la valeur 0 sur le plan $y=z$.

Enfin, restreignons $\rho(r)$ et $|\rho'(r)|$ à être suffisamment petites de telle sorte que soit vérifiée l'inégalité

$$\frac{\partial \chi(x, y, z)}{\partial x} + \frac{\partial \chi(x, y, z)}{\partial y} F(x, y) + \frac{\partial \chi(x, y, z)}{\partial z} F(x, z) \leq 0$$

pour $y \neq z$.

En effet, on peut écrire

$$\chi(x, y, z) = \int_{-1}^{+1} \int_{-1}^{+1} \int_{-1}^{+1} \psi(x + \rho\theta, y + \rho\theta_1, z + \rho\theta_2) d\theta d\theta_1 d\theta_2,$$

et, si (x, y, z) est un point de W tel que $y \neq z$, on aura, en prenant

un point voisin $(\bar{x}, \bar{y}, \bar{z})$ sur la courbe solution de (F) issue à droite du point (x, y, z) ($\bar{x} > x$), l'inégalité

$$\chi(x, y, z) \geq \chi(\bar{x}, \bar{y}, \bar{z}),$$

d'où découle l'inégalité précédente. Pour démontrer cette dernière inégalité, on prouvera que, pour $-1 \leq \theta, \theta_1, \theta_2 \leq 1$,

$$(1) \quad \begin{aligned} \phi(x + \rho\theta, y + \rho\theta_1, z + \rho\theta_2) &\geq \phi(\bar{x} + \bar{\rho}\theta, \bar{y} + \bar{\rho}\theta_1, \bar{z} + \bar{\rho}\theta_2) \\ [\rho = \rho(r) = \rho(|r - c|), \quad \bar{\rho} = \rho(\bar{r}) = \rho(|\bar{y} - \bar{z}|)]. \end{aligned}$$

Si $\bar{x} - x$ est assez petit, la courbe solution de (F) issue à droite du point $(x + \rho\theta, y + \rho\theta_1, z + \rho\theta_2)$ se prolonge, indifféremment pour $-1 \leq \theta, \theta_1, \theta_2 \leq 1$, jusqu'au point de l'abscisse (x) égale à $\bar{x} + \bar{\rho}\theta$, dont nous désignerons les coordonnées par $(\bar{x} + \bar{\rho}\theta, Y, Z)$, parce que $(\bar{x} + \bar{\rho}\theta) - (x + \rho\theta)$ est aussi petit¹; et nous avons, d'après les propriétés de $\partial(Q)$ [$= \varphi(x, y, z) = e^x \psi(x, y, z)$],

$$(2) \quad \phi(x + \rho\theta, y + \rho\theta_1, z + \rho\theta_2) \geq e^{(\bar{x} + \bar{\rho}\theta) - (x + \rho\theta)} \phi(\bar{x} + \bar{\rho}\theta, Y, Z)$$

et

$$(3) \quad \begin{aligned} &|\phi(\bar{x} + \bar{\rho}\theta, Y, Z) - \phi(\bar{x} + \bar{\rho}\theta, \bar{y} + \bar{\rho}\theta_1, \bar{z} + \bar{\rho}\theta_2)| \\ &\leq e^{-(\bar{z} + \bar{\rho}\theta_2)} \sqrt{[Y - (\bar{y} + \bar{\rho}\theta_1)]^2 + [Z - (\bar{z} + \bar{\rho}\theta_2)]^2}. \end{aligned}$$

Done, il suffit de démontrer que

$$(4) \quad e^{(\bar{x} + \bar{\rho}\theta) - (x + \rho\theta)} \phi(\bar{x} + \bar{\rho}\theta, Y, Z) \geq \phi(\bar{x} + \bar{\rho}\theta, \bar{y} + \bar{\rho}\theta_1, \bar{z} + \bar{\rho}\theta_2)$$

et

$$(5) \quad (\bar{x} + \bar{\rho}\theta) - (x + \rho\theta) > 0,$$

parce que les inégalités (2) et (4) entraînent (1). Or, l'inégalité (4) revient, au moyen de (3) et (5), à une autre telle que

$$(6) \quad \begin{aligned} &[(\bar{x} + \bar{\rho}\theta) - (x + \rho\theta)] \phi(\bar{x} + \bar{\rho}\theta, Y, Z) \\ &\geq e^{-(\bar{z} + \bar{\rho}\theta_2)} \sqrt{[Y - (\bar{y} + \bar{\rho}\theta_1)]^2 + [Z - (\bar{z} + \bar{\rho}\theta_2)]^2}. \end{aligned}$$

Pour réaliser l'inégalité (5), il suffit que l'on ait

$$\left| \frac{\bar{\rho} - \rho}{\bar{x} - x} \right| < 1,$$

mais ce premier membre tend, pour $\bar{x} \rightarrow x + 0$, vers la quantité

$$\begin{aligned} \left| \frac{d\rho}{dx} \right| &= \left| \frac{d\rho}{dr} \frac{dr}{dx} \right| = |\rho'(r)| \left| \frac{\partial r}{\partial y} \frac{dy}{dx} + \frac{\partial r}{\partial z} \frac{dz}{dx} \right| \\ &= |\rho'(r)| \cdot |F(x, y) - F(x, z)|, \end{aligned}$$

qui est plus petite que 1 si nous prenons $\rho'(r)$ assez petit pour $0 < r < \infty$, ce qui est possible. Quant à l'autre inégalité (6), c'est-à-dire

$$e^{\bar{x} + \bar{\rho}\theta} \phi(\bar{x} + \bar{\rho}\theta, Y, Z) \geq \frac{1}{(\bar{x} + \bar{\rho}\theta) - (x + \rho\theta)} \sqrt{[Y - (\bar{y} + \bar{\rho}\theta_1)]^2 + [Z - (\bar{z} + \bar{\rho}\theta_2)]^2},$$

dont le premier membre tend vers

1. Cf. la formule (5) suivante.

$$e^{x+\rho\theta}\phi(x+\rho\theta, y+\rho\theta_1, z+\rho\theta_2)=\varphi(x+\rho\theta, y+\rho\theta_1, z+\rho\theta_2)$$

pour $\bar{x} \rightarrow x+0$, uniformément par rapport à $(\theta, \theta_1, \theta_2)$, le second membre ne surpasse pas

$$\sqrt{\left(\frac{Y-(\bar{y}+\bar{\rho}\theta_1)}{(\bar{x}+\bar{\rho}\theta)-(x+\rho\theta)}\right)^2 + \left(\frac{Z-(\bar{x}+\bar{\rho}\theta_2)}{(\bar{x}+\bar{\rho}\theta)-(x+\rho\theta)}\right)^2},$$

où

$$\frac{Y-(\bar{y}+\bar{\rho}\theta_1)}{(\bar{x}+\bar{\rho}\theta)-(x+\rho\theta)} = \frac{Y-(y+\rho\theta_1)}{(\bar{x}+\bar{\rho}\theta)-(x+\rho\theta)} - \frac{\frac{\bar{y}-y}{\bar{x}-x} + \frac{\bar{\rho}-\rho}{\bar{x}-x}\theta_1}{1 + \frac{\bar{\rho}-\rho}{\bar{x}-x}\theta_1}$$

qui tend, pour $\bar{x} \rightarrow x+0$, vers

$$F(x, y) + \frac{d\rho}{dx}\theta_1 - \frac{F(x+\rho\theta, y+\rho\theta_1)}{1 + \frac{d\rho}{dx}\theta_1}$$

avec

$$\frac{d\rho}{dx} = \rho'(r) \frac{y-z}{r} [F(x, y) - F(x, z)] \quad (r = |y-z|),$$

uniformément par rapport à $(\theta, \theta_1, \theta_2)$, et de même pour

$$\frac{Z-(\bar{z}+\bar{\rho}\theta_2)}{(\bar{x}+\bar{\rho}\theta)-(x+\rho\theta)}.$$

Ces dernières quantités deviennent inférieures, en module, à une fonction positive et continue de $r = |y-z| > 0$, et arbitraire, par un choix convenable de $\rho(r)$, grâce à la continuité uniforme de F . Cependant, la limite précédente $\varphi(x+\rho\theta, y+\rho\theta_1, z+\rho\theta_2)$ est, en supposant $\rho(r) < \frac{r}{2}$ par exemple, supérieure à une fonction positive et continue de r pour $r > 0$, parce que la fonction $\varphi(x, y, z)$ est continue dans W_1 (frontière incluse) et positive pour $r > 0$. En somme, il suffit de prendre $\rho(r)$ et $|\rho'(r)|$ suffisamment petits.

4. La fonction $\chi(x, y, z)$ remplit toutes les conditions exigées à $\Phi(x, y, z)$ sauf l'existence et la continuité des dérivées pour $y=z$. Pour compléter ce dernier point, il suffit d'adopter¹, au lieu de $\chi(x, y, z)$, la fonction $\omega[\chi(x, y, z)]$ de χ , où

$$\omega(u) = \int_0^u \omega'(u) du, \quad \omega'(u) > 0 \quad (u > 0),$$

la dérivée $\omega'(u)$ étant continue pour $u \geq 0$ et infiniment petite avec u de telle manière que

1. Cf. loc. cit. (1941), p. 231.

$$\omega'(u) = o\left(\frac{1}{\max_{\chi(x, y, z) = u} [|\chi'_x(x, y, z)|, |\chi'_y(x, y, z)|, |\chi'_z(x, y, z)|]}\right).$$

Alors la fonction

$$\Phi(x, y, z) = \omega[\chi(x, y, z)]$$

possède les dérivées continues et nulles pour $y=z$, et satisfait tout à fait à l'énoncé du Théorème.

C. q. f. d.

II.—Exemples.

L'existence d'une telle fonction Φ , comme dans l'énoncé du Théorème, peut se justifier directement pour les cas particuliers suivants :

1. Dans le cas de la condition de Lipschitz :

$$|F_i(x, y_1, \dots, y_n) - F_i(x, z_1, \dots, z_n)| \leq K \sqrt{(y_1 - z_1)^2 + \dots + (y_n - z_n)^2} \\ (i = 1, 2, \dots, n),$$

on peut poser

$$\Phi(x, y_1, \dots, y_n) = e^{-2nKx} [(y_1 - z_1)^2 + \dots + (y_n - z_n)^2].$$

2. Un cas d'une équation différentielle ordinaire sans points de Peano qui ne rentre pas à celui de Lipschitz est donné par l'équation

$$\frac{dy}{dx} = -\frac{f'_x(x, y)}{f'_y(x, y)}$$

où $f(x, y)$ est une fonction douée de dérivées continues $f'_x(x, y)$ et $f'_y(x, y)$, $f'_y(x, y) \neq 0$, dans un domaine. On a, en effet, la solution générale

$$f(x, y) = \text{const.}$$

Alors, on peut prendre, dans l'énoncé du Théorème,

$$\Phi(x, y, z) = [f(x, y) - f(x, z)]^2.$$

3. Un autre exemple intéressant est dû à M. Carathéodory¹; c'est le système suivant :

$$\frac{dy}{dx} = y', \quad \frac{dy'}{dx} = \frac{\partial f(x, y)}{\partial x} + \frac{\partial f(x, y)}{\partial y} y',$$

où la fonction $f(x, y)$ est supposée continue, avec ses dérivées premières, dans un domaine. Si nous supposons ces dérivées bornées, en module, par L , on peut adopter, dans le Théorème ($y_1 = y, y_2 = y'$), que

$$\Phi(x, y, y', z, z') = e^{-4Lx} \{ 4L^2(y - z)^2 + [y' - f(x, y) - z' + f(x, z)]^2 \},$$

parce que

$$\frac{\partial \Phi}{\partial x} + \frac{\partial \Phi}{\partial y} y' + \frac{\partial \Phi}{\partial y'} \left(\frac{\partial f(x, y)}{\partial x} + \frac{\partial f(x, y)}{\partial y} y' \right)$$

1. Variationsrechnung (1936), p. 17.

$$\begin{aligned}
& + \frac{\partial \Phi}{\partial z} z' + \frac{\partial \Phi}{\partial z'} \left(\frac{\partial f(x, z)}{\partial x} + \frac{\partial f(x, z)}{\partial z} z' \right) \\
& = 4Le^{-4Lx} \{ -4L^2(y-z)^2 - [y' - f(x, y) - z' + f(x, z)]^2 \\
& \quad + 2L(y-z)(y' - z') \} \\
& = 4Le^{-4Lx} \{ -4L^2(y-z)^2 - (y' - z')^2 + 2(y' - z')[f(x, y) - f(x, z)] \\
& \quad - [f(x, y) - f(x, z)]^2 + 2L(y-z)(y' - z') \} \\
& \leq 4Le^{-4Lx} \{ -4L^2(y-z)^2 - (y' - z')^2 + 2L|y' - z'| \cdot |y - z| \\
& \quad + 2L|y - z| \cdot |y' - z'| \} \\
& = -4Le^{-4Lx} (2L|y - z| + |y' - z'|)^2 \\
& \leq 0.
\end{aligned}$$

The Compressibility of Solid Elements as Expressed in Terms of their Melting Points and Atomic Volumes

by Usaburo Yoshida and Yosio Masui

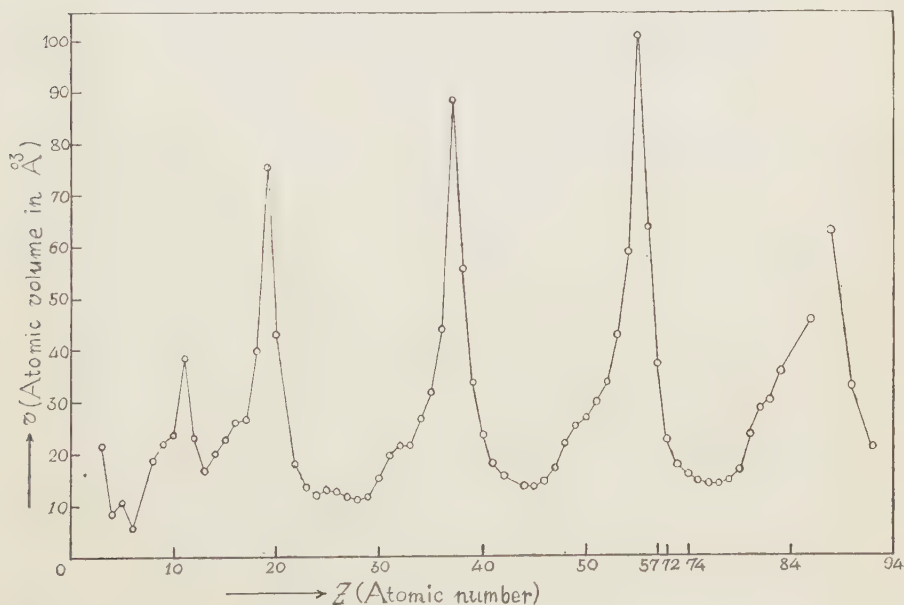
(Received August 9, 1941)

Abstract

The compressibility of solid elements is found to be expressed approximately in terms of their melting points, atomic volumes and atomic numbers by an empirical formula, which is more reasonable than that proposed by Richards.

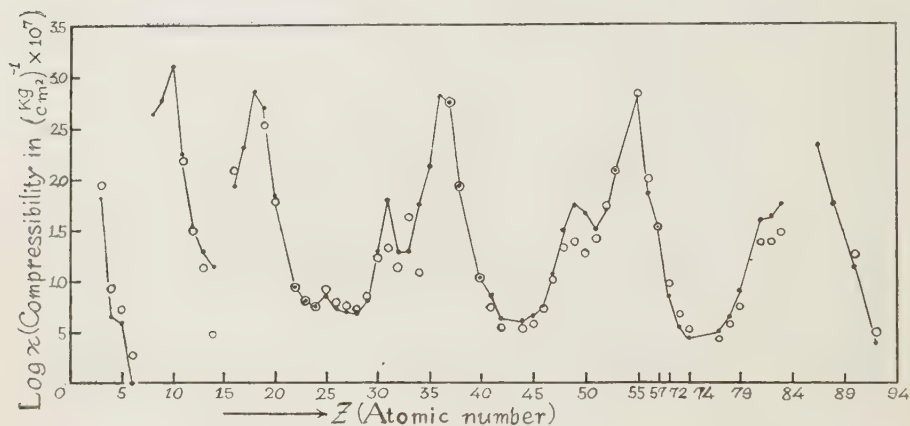
The compressibility of solid elements is a strongly periodic function of the atomic number, as was first pointed out by Richards. Besides the compressibility, the atomic volume of solid elements is also very clearly periodic with respect to the atomic number, as is seen in Fig. 1. In this and in the following three figures, all the rare earth elements other than lanthanum are omitted, so as to be in accord

Fig. 1.



with the periodic table of the elements; and the element hafnium of the atomic number 72 is arranged next to lanthanum whose atomic number is 57. As is seen in Fig. 1, the periodicity in the atomic volume is especially regular with the elements having the atomic numbers higher than 19, which belong to the long periods in the periodic table. The compressibilities of solid elements, which are measured at room temperature, are represented by small circles in Fig. 2. In this figure the logarithm to the base 10 of the compressibility is plotted, in order to get a manageable scale, against atomic number. The periodic change of the compressibility with atomic number

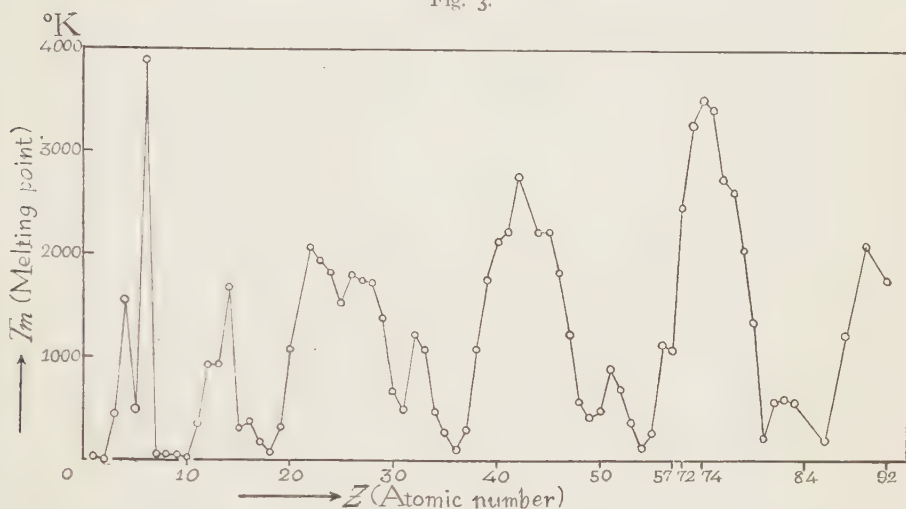
Fig. 2.



is also well revealed especially with the elements in the long periods; and it runs similarly in main features with atomic volume, by taking maxima at the positions of the alkali-metals and minima at the intermediate positions. However, this similarity is not perfect; and the general tendency of the compressibility to decrease in its value at the positions about its minima with increase of atomic number does not accord with the increase of the atomic volume about the positions of its minima with increase of atomic number. This shows that the compressibility of the solid elements can not be represented as a function of the atomic volume alone.

Besides the atomic volume, the melting point of the elements is also related to the compressibility, because the hardness is generally higher for an element whose melting point is higher. Fig. 3 shows the relation between the melting point and the atomic number of the elements. A general periodicity is also detected in this case. Alkali-

Fig. 3.



metals occupy the positions next to the minima which are occupied by rare gases, and the intermediate elements lie at the positions about the maxima. Moreover, the maxima of the melting points increase generally with atomic number. Taking this fact into consideration, the writers assumed that the compressibility κ is directly proportional to a certain power n of the atomic volume v and is inversely proportional to the melting point T_m , expressed in absolute scale. In order to get the value of n , κT_m , the products of the observed values of κ and T_m for the elements, were compared with their observed values of v , by plotting the logarithms of κT_m and v in a graph; and from an approximately linear relation between the values of these logarithms the value of n was found to be about 1.5. The proportionality thus found between κT_m and $v^{1.5}$ is only an approximation; and a small systematic increase of the value of $v^{1.5}/\kappa T_m$ with increase of the atomic number Z was clearly detected. Thus $v^{1.5}/\kappa T_m$ was assumed to be proportional to $\alpha(1+\beta Z)$, and the values of α and β were obtained by plotting the values $v^{1.5}/\kappa T_m$ and Z in a graph.

The observed values of v , T_m , κ and $\log \kappa$ for the elements are tabulated in Tables I_a and I_b. The values of the melting point T_m were taken from Landolt-Boernstein's "Physikalisch-chemische Tabellen" and others. The values of the atomic volume v expressed in the unit of $\text{\AA}^3$ per atom were taken mostly from Masing's "Handbuch der Metallphysik" (Bd. I, p. 43-62) for the elements whose atomic volumes were determined from their crystal structures; and for some other

Table I a.

Element	Atomic number Z	Atomic volume v in $\text{\AA}^3$	Melting point T_m in $^\circ\text{K}$	Compres- sibility $\kappa_{\text{obs.}}$ in $\left(\frac{\text{kg}}{\text{cm}^2}\right)^{-1} \times 10^7$	$\kappa_{\text{calc.}}$	$\log \kappa_{\text{calc.}}$	$\log \kappa_{\text{obs.}}$
H	1	37.3	15	—	—	—	—
He	2	3.5	1	—	—	—	—
Li	3	20.7	453	87.0	65.7	1.818	1.94
Be	4	8.2	1551	8.6	4.67	.669	.934
B	5	10.3	2573	5.5	3.96	.598	.740
C (graphite)	6	8.9	3870	1.8	.98	1.991	.255
N	7	46.2	62	—	—	—	—
O	8	18.4	55	—	421	2.624	—
F	9	22.0	50	—	594	2.774	—
Ne	10	23.1	24	—	1313	3.118	—
Na	11	38.1	371	156	178.7	2.252	2.193
Mg	12	23.0	923	29.5	33.1	1.520	1.47
Al	13	16.5	931	13.4	19.5	1.29	1.127
Si	14	20.0	1693	3.1	14.25	1.154	.491
S	16	26	390	129	88.4	1.946	2.111
Cl	17	26.6	172	—	204	2.310	—
A	18	39.8	83	* —	750	2.875	—
K	19	75.8	337	357	499	2.698	2.553
Ca	20	43	1078	57	64.9	1.812	1.756
Ti	22	17.7	2073	8.0	8.55	.932	.903
V	23	13.7	1953	6.1	6.14	.788	.785
Cr	24	11.9	1823	5.2	5.28	.723	.716
Mn	25	13.3	1518	7.9	7.4	.869	.898
Fe	26	12.2	1803	5.9	5.47	.738	.771
Co	27	11.2	1763	5.4	4.86	.687	.732
Ni	28	10.9	1725	5.3	4.65	.667	.724
Cu	29	11.8	1356	7.2	6.62	.821	.857
Zn	30	15.0	693	16.9	18.2	1.26	1.228
Ga	31	19.6	303	20	62.2	1.794	1.301
Ge	32	21.9	1231	13.8	17.8	1.25	1.14
As	33	21.7	1090	44	19.5	1.29	1.643
Se	34	26.9	493	11.8	59.2	1.772	1.072
Br	35	31.7	267	—	138	2.14	—
Kr	36	43.7	104	—	660	2.820	—
Rb	37	88.7	312	520	543	2.735	2.716

Table I b.

Element	Atomic number Z	Atomic volume v in $\text{\AA}^3$	Melting point T_m in $^\circ\text{K}$	Compress- ibility $\kappa_{\text{obs.}}$ in $\left(\frac{\text{kg}}{\text{cm}^2}\right)^{-1} \times 10^7$	$\kappa_{\text{calc.}}$	$\log \kappa_{\text{calc.}}$	$\log \kappa_{\text{obs.}}$
Sr	38	56	1073	82	78.3	1.894	1.914
Y	39	33.7	1763	—	—	—	—
Zr	40	23.4	2133	11	10.4	1.017	1.041
Nb	41	18.0	2223	5.7	6.67	.824	.756
Mo	42	15.5	2773	3.6	4.23	.626	.556
Ru	44	13.4	2223	3.4	4.15	.618	.531
Rh	45	13.6	2243	3.7	4.19	.622	.568
Pd	46	14.5	1823	5.3	5.6	.748	.724
Ag	47	17.0	1233	9.9	10.4	1.017	.996
Cd	48	21.4	594	22.5	30.2	1.48	1.343
In	49	25.1	427	25.0	52.8	1.723	1.398
Sn	50	27.0	505	18.8	49.0	1.69	1.274
Sb	51	29.7	903	27.0	31.6	1.50	1.431
Te	52	33.7	723	50.8	47.1	1.673	1.706
I	53	42.5	387	127	123.5	2.092	2.104
Xe	54	59.0	133	—	585	2.767	—
Cs	55	100.7	302	700	638	2.805	2.845
Ba	56	63.1	1123	102	75.3	1.877	2.009
La	57	37.0	1083	35	34.8	1.542	1.544
Hf	72	22.5	2480	9.0	7.16	.855	.954
Ta	73	17.7	3303	4.8	3.68	.566	.681
W	74	15.8	3543	3.2	2.87	.458	.505
Re	75	14.8	3440	—	—	—	—
Os	76	14.0	2773	—	—	—	—
Ir	77	14.0	2623	2.7	3.17	.501	.431
Pt	78	14.9	2048	3.6	4.42	.645	.556
Au	79	16.9	1336	5.8	8.09	.908	.763
Hg	80	23.2	234	37	—	—	—
Tl	81	28.5	573	22.8	40.7	1.610	1.358
Pb	82	30.0	600	23.7	41.4	1.617	1.375
Bi	83	35.2	545	29.2	57.7	1.761	1.465
Rn	86	45.6	202	—	224	2.350	—
Ra	88	62.3	1233	—	57.7	1.761	—
Th	90	32.8	2113	18.2	14.0	1.146	1.26
U	92	20.1	1773	9.7	8.34	.921	.987

elements they were calculated from the values of the densities and the molecular weights. As the compressibility of the solid elements which is measured at room temperature changes with pressure, its limiting value at zero pressure is adopted, and the values expressed in the unit of $\left(\frac{Kg}{cm^2}\right)^{-1} \times 10^7$ are tabulated in Tables I_a and II_b. These are taken from Bridgman's "The Physics of High Pressure". By taking the units of v and the compressibility κ as above, the empirical formula obtained for the relation between κ , v , T_m and Z became

$$\kappa = \frac{v^{1.5}}{0.003(1 + 0.0175Z)T_m}$$

The values of κ and $\log \kappa$ which are calculated by this formula from the values of v , T_m and Z are tabulated in the 6th and 7th columns of the tables, and the values of $\log \kappa$ for the observed values of κ are given in the last column of the tables. The values of $\log \kappa$ thus calculated are represented by the dots in Fig. 2, where the successive dots are connected by the straight lines. When the positions of dots are compared with those of small circles representing the observed values of $\log \kappa$ in Fig. 2, we see that the agreement between the observation and the calculation is, in main features, rather satisfactory for this kind of phenomenon, because the compressibility changes with temperature and pressure and is accompanied by a considerable amount of errors in its measurement. The unsatisfactory agreement is met within the elements belonging to the short periods in the periodic table, in the Ga ($Z=31$), Ge ($Z=32$), As ($Z=33$), Se ($Z=34$) sequence, in the Cd ($Z=48$), In ($Z=49$), Sn ($Z=50$) sequence, and in the Tl ($Z=81$), Pb ($Z=82$), Bi ($Z=83$) sequence.

There is no direct measurement reported on the compressibilities of rare gases, but they are supposed by Bridgman¹ to be much higher than those of other elements. This suggestion is in accord with the present results. The compressibilities calculated by the present formula for Ne, Ar and Kr occupy the maximum positions as is seen in Fig. 2, and they are higher than those of corresponding alkali-metals which take the maximum positions among the measured values. For Xe, its calculated compressibility is almost the same as that observed for the following element Cs.

Prior to the present writers, a similar empirical formula representing the compressibility in terms of the atomic volume, melting point

1. Bridgman: The Physics of High Pressure, p. 165 (1931).

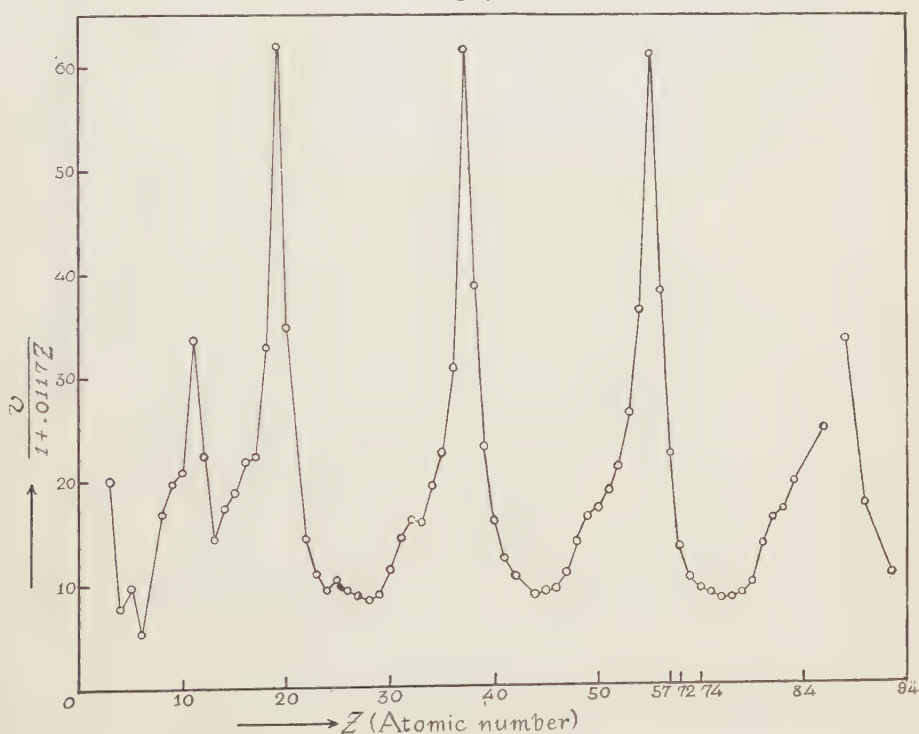
and the specific gravity of the element had been proposed by Richards¹. His formula is as follows

$$\kappa = 0.00021 \frac{A}{S^{0.25}(T_m - 50)},$$

where A is the atomic volume, and S is the specific gravity. Richards' formula can represent the observed values of the compressibilities equally well as that proposed by the writers; but the applicability of his formula is limited for the elements whose melting point is higher than 50°K. With the formula proposed by the writers this defect is removed, and it can be applied generally for all the elements.

It has already been stated that the periodicity in the atomic volume is especially regular with the elements which belong to the long periods in the periodic table. However, this regularity is not entirely perfect; and we can detect, in Fig. 1, a systematic and linear increase in the value of the atomic volume with increase of the atomic number. This linear increase of the atomic volume was found to be well

Fig. 4.



1. Sachs: Mechanische Technologie der Metalle, p. 226 (1925).

systematized by adopting, instead of the actual atomic volume v , the reduced atomic volume v_r , which is connected with v by the relation

$$v_r = \frac{v}{1 + 0.0117Z}$$

where Z represents the atomic number as before. The relation between v_r and Z is plotted in Fig. 4, and an almost perfect periodicity of the reduced atomic volume in the long periods is obtained in this figure: the corresponding elements in different periods take almost the same reduced atomic volume.

In the case of compressibility the value of αT_m was found to be proportional to $v_r^{1.5}/(1 + 0.0175Z)$. If we use the reduced atomic volume v_r instead of v , we have

$$\alpha_r^{1.5} = \frac{v_r^{1.5}}{(1 + 0.0117Z)^{1.5}} \div \frac{v_r^{1.5}}{1 + 0.0175Z}$$

and consequently the empirical formula representing the compressibility becomes more simple, as

$$\alpha = \frac{\alpha_r^{1.5}}{0.003 T_m}.$$

The Corresponding Temperature of Liquid Elements and its Bearing on the Melting Points and the T_2 Points

by Usaburo Yoshida

(Received August 30, 1941)

Abstract

From Trouton's rule of the approximate proportionality between the latent heat of vaporization L_v , per gram molecule of the elements and the normal boiling point T_b expressed in the absolute temperature scale, the mean value of the ratio L_v/T_b was found to be 27.4 cal per degree. The temperature $T_{c. h. p.}$ obtained by dividing the observed value of L_v of an element by 27.4 is called, the corresponding boiling point of the element, which is somewhat different from the normal boiling point. Relying upon Young's formula for the saturated vapour pressure the ratio of the vapour pressure at the corresponding boiling point of a liquid to that it would have to acquire at the infinitely high temperature becomes the same for all substances. By plotting in a graph the correlation among the corresponding boiling points, the melting points and the T_2 points of monoatomic elements, the correspondency of the state of different elements and the unaccordance of their melting points with any simple energy law were investigated.

Introduction

In a paper¹ published recently the writer applied van't Hoff's reaction isochore to the equilibrium between the cybotactic crystals and the free molecules of a substance in liquid state; and by taking the number of constituent molecules of a cybotactic crystal as infinite the case was transferred to the equilibrium between the crystal nuclei and the free liquid molecules of a substance in its super-cooled state. By denoting the absolute temperature by T and the degree of decomposition of the crystal nuclei by x , the change of $\frac{dx}{dT}$ with temperature for monoatomic elements was investigated; and it was found that the temperature T_2 at which $\frac{dx}{dT}$ is maximum has a simple and important relation with the latent heat of fusion referred to one gram atom for the majority of elements, excepting bismuth and gallium. When the

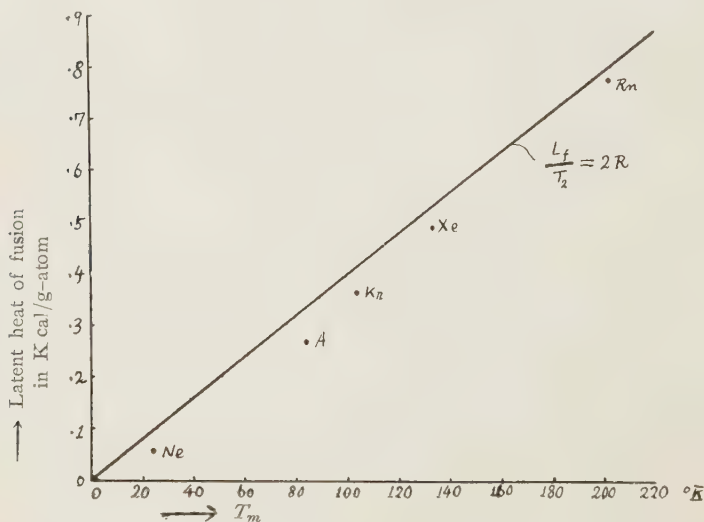
1. U. Yoshida: These Memoirs, A, **24**, 121 (1941).

latent heat of fusion of a monoatomic element referred to one gram atom is represented by L_f calorie, the T_2 point was found to be given by

$$\frac{L_f}{T_2} = 2R, \dots\dots\dots (1)$$

where R is the gas constant, and takes the value of 1.985 calorie per degree. This relation will be called "the T_2 -point-law" hereafter. Next it was found that when the temperature is raised the value of $\frac{dx}{dT}$ falls to zero abruptly at the limit when x approaches to 1 at a certain temperature. This temperature was taken as the melting point T_m of the substance, because the crystal nuclei can exist in equilibrium only in lower temperatures than this but not above it. As the T_2 point occurs at a smaller value of x than 1 for the majority of monoatomic elements excepting bismuth and gallium, this point is usually lower than T_m . The T_2 -point-law and this relation between T_2 and T_m for the rare gases in their super-cooled liquid state are

Fig. 1



shown by Fig. 1, as a supplement to Fig. 10 of the former paper. In this figure the latent heat of fusion L_f is taken as ordinate and the melting point T_m and the T_2 point as abscissa, and the T_2 -point-law is represented by the straight line. As is seen in the figure all the dots which represent the observed values of L_f and T_m occupy the positions just on the right hand side of the straight line. This shows

that T_m is slightly higher than T_2 for every substance as was deduced theoretically.

**Trouton's Rule and the Graphical Representation of the
Latent Heats of Vaporization, Boiling Points, T_m
and T_2 Points of Monoatomic Elements**

As is stated above, if we imagine the state of super-cooled-liquid of a substance, we can follow the temperature change of its property even below the melting point without any discontinuity, and a comparison of corresponding states of different substances in wider temperature range becomes thus possible. For the present, only monoatomic elements which are provided with necessary data are investigated; and if not particularly noticed, monoatomic elements will be meant by the substances in the present paper. The observed values for many substances of normal boiling point T_b , latent heat of vaporization L_v at T_b referred to one gram atom, melting point T_m and latent heat of fusion L_f at T_m referred to one gram atom are taken mostly from the International Critical Table, and are tabulated in Table I. The values of T_2 , which are given in the 6th column of Table I are calculated by means of the T_2 -point-law from the observed values of L_f for the majority of the elements; but for bismuth it was taken to be the same as its melting point. The correlation among the T_2 points, melting points, boiling points and the latent heats of vaporization at the boiling points is shown in Fig. 2 for most of the elements and in Fig. 3 for the rare gases. In these figures the latent heat of vaporization is taken as ordinate and the temperature as abscissa, and the boiling points are represented by the dots. As is seen in Fig. 2 most of the dots take the positions near the straight line passing through the origin of coordinates; showing that the values of L_v/T_b for different substances are approximately the same in accord with Trouton's rule. The straight line OA in Fig. 2 is so drawn that the value of L_v/T_b is the same as the mean for the elements having comparatively high boiling points and takes the value of 27.4. Thus the straight line OA may be called the "mean boiling point line"; but the writer prefers to call it "the corresponding boiling point line" by the reason as will become clear later. Next vertical lines were drawn to pass through every one of the dots, and from their intersections with the straight line OA horizontal lines were drawn. On each of these horizontal lines, the T_2 point and the melting point T_m of the corresponding element were marked by a small circle and a

Table I

Element	Normal boiling point T_b in °K {(S) : Sublimation}	Latent heat of vaporization L_v at T_b in $\frac{\text{K cal}}{\text{g-atom}}$	Melting point T_m in °K	Heat of fusion L_f at T_m in $\frac{\text{K cal}}{\text{g-atom}}$	T_2 in °K	$T_{c. b. p.}$ in °K
A	87	1.502	84	0.268	67.5	54.9
Ag	2223	59.5	1233	2.63	663	2175
Al	2073	53.7	933	1.91	482	1960
As (metallic)	888(S)	33.2(S)	1087($\frac{36}{\text{atms}}$)			1210
Au	2873	88.0	1336	3.18	803	3220
Bi	1723	46.1	544	2.60	544	1685
Cd	1040	25.6	594	1.48	374	935
Co	3173	90.8	1753	3.44	868	3120
Cr	2473	76.5	1888	1.65	416	2800
Cs	943	17.45	299	0.501	126	637
Cu	2573	70.6	1356	2.75	693	2580
Fe	3273	90.8	1808	2.68	776	3315
He	4	0.024	< 0.8			
Hg	630	14.2	234	0.556	140	519
K	1033	20.1	335	0.57	144	735
Kr	121	2.24	104	0.36	91	82
Li	1470	40.6	459	0.835	211	1482
Mg	1383	62.6	924	1.7	429	2285
Mn	2173	57.4	1533	2.01	507	2097
Na	1153	25.1	371	0.633	159	915
Ne	27	0.416	24	0.057	14.4	15.2
Ni	3173	90.6	1725	4.33	1090	3310
Pb	1893	46.1	600	1.12	282	1682
Pt	4573	124.0	2028	5.25	1325	4530
Rb	973	17.7	312	0.52	131	646
Rn	211	4.3	202	0.776	196	157
Sn	2533	77.6	505	1.67	421	2835
Xe	164	3.2	133	0.49	124	117
Zn	1180	23.7	692	1.7	429	865

cross respectively. Fig. 3, which is for rare gases, is drawn in a magnified scale entirely in the same manner as Fig. 2. From these figures we note that, while the crosses are distributed widely apart, the small circles rather crowd together near a straight line passing through the origin of coordinates.

With metallic arsenic, the vapour pressure due to sublimation from the solid is very high, and it boils under atmospheric pressure,

Fig. 2

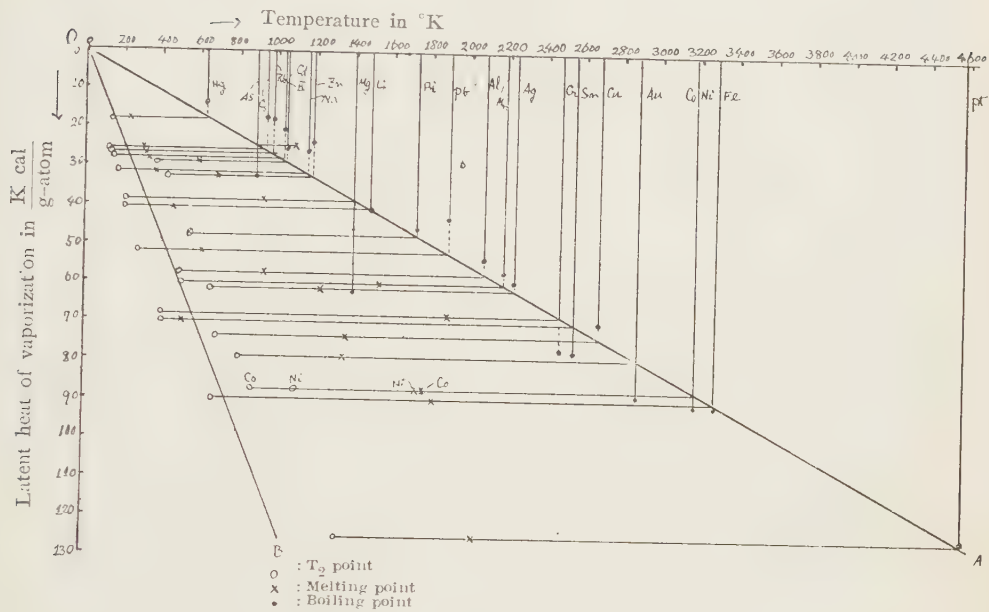
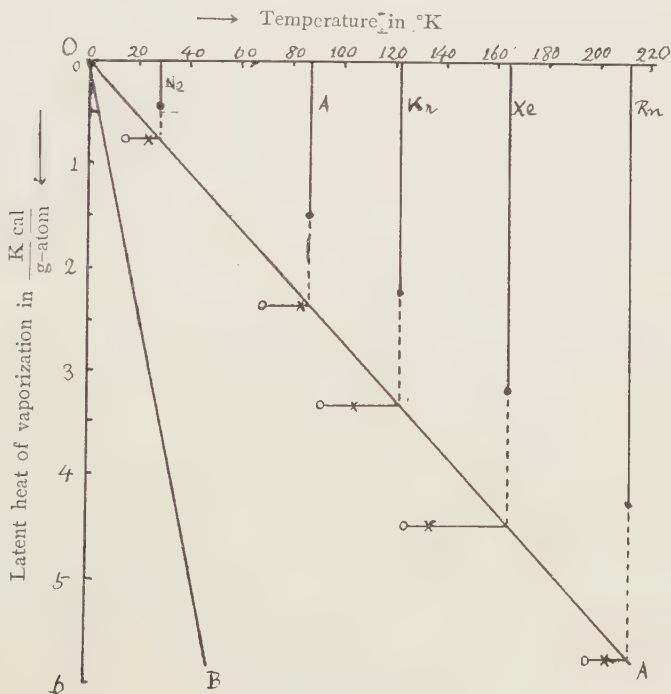


Fig. 3



from the solid state instead of from the liquid. This is indicated by inserting (s) in Table I. Thus the latent heat of vaporization L_v at T_b as is given in the table is somewhat greater than that in the case of the vaporization from the liquid. But the writer regards the former as approximately the same with the latter, and he treats arsenic entirely in the same manner as the other elements. The vapour pressure at the triple point of arsenic is so high as 36 atmospheres, the temperature at this point being 1087°K . Consequently if we take the melting point of this element as 1087°K , it comes to be higher than the boiling point 888°K , in contrary to the ordinary case. This apparent contradiction is caused by the conventional definition of the normal boiling point in taking it as the temperature at which the vapour pressure attains the standard atmospheric pressure. Instead of it, if we take a sufficiently high vapour pressure as that at the boiling point, then the boiling point rises correspondingly and comes to be higher than the melting point, in right order, as the melting point is only slightly affected by the change of pressure.

Vapour Pressure at the Melting Point

The vapour pressure of a substance at its melting point is considerable when the melting point is very close to its boiling point as in the case of rare gases. On the contrary when the melting point of a substance is very much lower than its boiling point, its vapour pressure at the melting point decreases so remarkably as is impossible to be measured as in the case of most metals. In the latter case the vapour pressure at the melting point is only to be estimated by extrapolation from its values measured at much higher temperatures. In doing so Young's formula representing the vapour pressure as a function of temperature was used. If we take the latent heat of vaporization L_v as approximately constant irrespectively of temperature, then Young's formula can be written as

$$p = p_0 e^{-\frac{L_v}{RT}} \dots\dots\dots (2)$$

where p represents the vapour pressure at the temperature T , and p_0 that which the substance would take at infinitely high temperature if the value of L_v is supposed to remain constant. By taking logarithm the equation (2) becomes

$$\log_{10} p = \log_{10} p_0 - \frac{L_v}{RT} \log_{10} e,$$

and can be rewritten as

$$\log_{10} p = B - \frac{A}{T} \dots\dots\dots (3)$$

where *A* and *B* are constants.

For many metals their vapour pressures were measured in a range of temperature much higher than their melting points, and the numerical values of *A* and *B* were determined. By using these values

Table II

Element	Vapour pressure <i>p_m</i> in mm Hg at <i>T_m</i>	log ₁₀ <i>p_m</i>	$\frac{T_b}{T_m}$	$\frac{L_f}{L_v}$	$\frac{T_{c. b. p.}}{T_m}$
A	512(Trip.)	+ 2.71	1.035	0.178	0.654
Ag	1.51 × 10 ⁻²	− 1.82	1.80	0.0441	1.76
Al	—	—	2.20	0.0356	2.10
As	2.74 × 10 ⁴ (Trip.)	+ 4.44	0.818	—	1.11
Au	6.21 × 10 ⁻⁶	− 5.21	2.15	0.0361	2.41
Bi	5.1 × 10 ⁻¹¹	− 10.29	3.17	0.0564	3.10
Cd	1.07 × 10 ⁻¹	− 0.971	1.75	0.0578	1.57
Co	2.35 × 10 ⁻²	− 1.63	1.81	0.0379	1.78
Cr	—	—	1.32	0.0216	1.48
Cs	1.4 × 10 ⁻⁶	− 5.85	3.16	0.0287	2.13
Cu	2 × 10 ⁻⁶	− 5.69	1.90	0.0389	1.91
Fe	3.47 × 10 ⁻²	− 1.46	1.81	0.0295	1.83
Hg	1.2 × 10 ⁻⁶	− 5.91	2.69	0.0391	2.22
K	9.12 × 10 ⁻⁷	− 6.04	3.09	0.0284	2.195
Kr	133(Trip.)	+ 2.124	1.165	0.161	0.789
Li	—	—	3.20	0.0206	3.24
Mg	1.95 × 10 ⁻²	− 1.71	1.50	0.0272	2.47
Mn	1.63	+ 0.21	1.42	0.0350	1.37
Na	1.05 × 10 ⁻⁷	− 6.98	3.11	0.0252	2.47
Ne	300	+ 2.477	1.13	0.137	0.633
Ni	1.78 × 10 ⁻²	− 1.75	1.84	0.0477	1.92
Pb	2.9 × 10 ⁻⁹	− 8.53	3.16	0.0243	2.81
Pt	2.1 × 10 ⁻⁵	− 4.68	2.26	0.0423	2.23
Rb	1.9 × 10 ⁻⁶	− 5.72	3.12	0.0294	2.07
Rn	500(Trip.)	+ 2.70	1.04	0.180	0.778
Sn	4.7 × 10 ⁻²⁶	− 25.33	5.03	0.0215	5.61
Xe	80	+ 1.90	1.23	0.153	0.88
Zn	1.5 × 10 ⁻¹	− 0.82	1.71	0.0719	1.25
Mean value				0.0318	

of A and B , given in the International Critical Table, the writer calculated by extrapolation the vapour pressures and their logarithms at the melting points of metals; and they are tabulated in Table II. As the melting points were very much lower than the temperature ranges in which the vapour pressures were measured the values of vapour pressures and their logarithms given in Table II are considered to contain considerable errors of course. However, for an investigation upon their orders of magnitude they will still be of use sufficiently. For the vapour pressures of the rare gases and arsenic values directly measured at the melting point or at the triple point are available. As the melting point is very near to the triple point, the writer regards for the present that the vapour pressures at the triple points are the same as those at the melting points, and they are given in Table II by noting them with (Trip.).

It has already been stated that the vapour pressure of a substance at its melting point gets the smaller as the greater apart the melting point is removed from its boiling point. Now let us consider this point quantitatively. As is stated before the vapour pressure of a substance at a temperature T can be expressed approximately by equation (2). At the melting and boiling points it becomes respectively

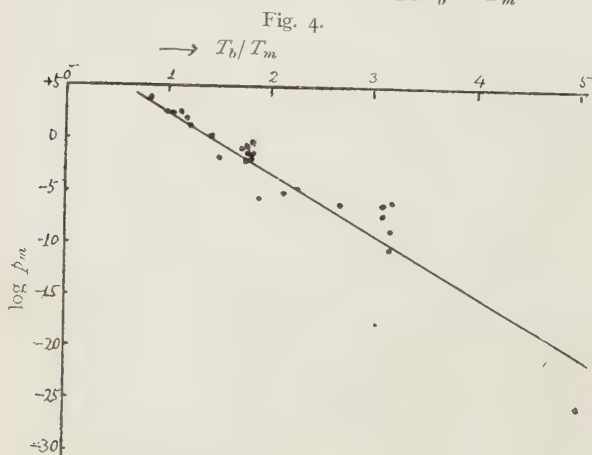
$$p_m = p_0 e^{-\frac{L_v}{RT_m}},$$

and

$$p_b = p_0 e^{-\frac{L_v}{RT_b}},$$

where p_m and p_b represent the vapour pressures at the melting and boiling points respectively. Dividing one with the other and then taking the logarithm we get

$$\log_{10} p_m = \log_{10} p_b - \left\{ \frac{L_v}{RT_b} \left(\frac{T_b}{T_m} - 1 \right) \right\} \log_{10} e \dots\dots\dots (4)$$



If Trouton's rule is valid for different substances, we can see from equation (4) that the values of $\log_{10} p_m$ for different substances must decrease linearly with the values of T_b/T_m . This point was examined by representing the values of $\log_{10} p_m$ and T_b/T_m ,

given in Table II, by the dots plotted in Fig. 4; and an approximately linear relation between $\log_{10} p_m$ and T_b/T_m was obtained. The straight line shown in Fig. 4 is so drawn that it passes through the average position of the dots. The average value of L_v/T_b obtained from the inclination of the straight line is 27.0, and is in good accord with 27.4 which is given above.

The Corresponding Temperature of Different Substances in the Liquid State, and the Situation of their Boiling, Melting and T_2 Points

The values of the vapour pressure, p_0 , which a liquid would take at infinitely high temperature is different according to the kind of substances as will be seen from the deviation of the normal boiling points from Trouton's rule. However, at the normal boiling points all substances must possess the same normal atmospheric pressure. Considered from this angle the normal boiling points of different substances can not be accepted as physically corresponding temperatures in their liquid state. It seems more reasonable, from the theoretical point of view, to define the corresponding temperatures of different liquid substances as those at which the ratio p/p_0 is constant. If we take the latent heat of vaporization L_v of a substance as approximately constant independent of the temperature change, then the value p/p_0 is determined, by the aid of Young's formula, only by the value of L_v/T irrespectively of the kind of substances. Hence the writer will define the corresponding temperatures as those at which L_v/T is constant for different substances. It has already been stated that the average value of L_v/T_b for many elements having comparatively high boiling points is 27.4. Accordingly, the temperatures determined by equating L_v/T to 27.4 and by assigning to L_v the observed values will be called "the corresponding boiling points" and they will be represented by $T_{c. b. p.}$. The values of $T_{c. b. p.}$ thus calculated for different elements are given in the last column of Table I. As the values of p_0 are different for different elements the actual values of the vapour pressure at the corresponding boiling points are different with the kind of elements. However, the mean of these different actual values will be very close to the normal atmospheric pressure, because the proportional constant 27.4 of $L_v/T_{c. b. p.}$ was obtained by taking the average of the values of L_v/T_b for the elements having comparatively high boiling points.

Defining the corresponding boiling point as above, the writer re-

plotted the correlation, as seen in Figs. 2 and 3, among the values of

Fig. 5

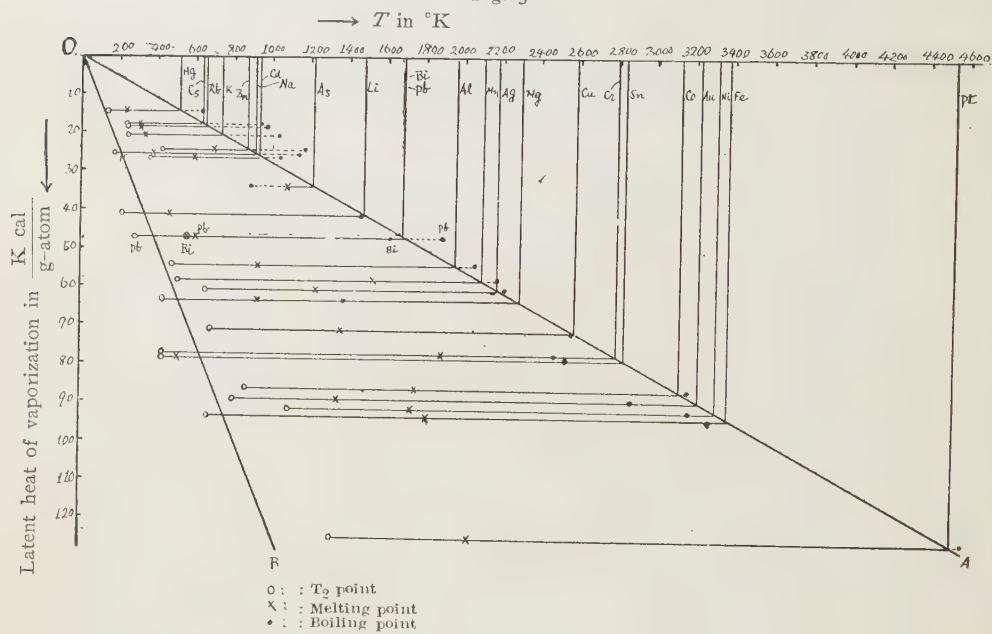
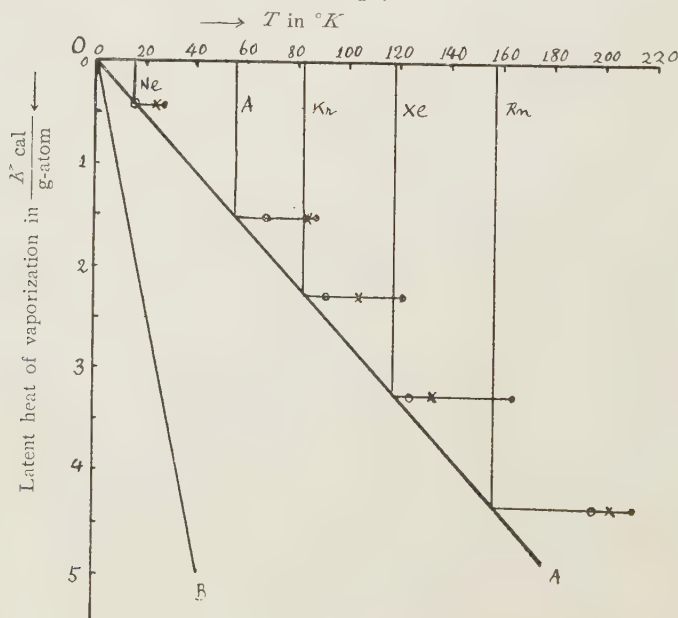


Fig. 6

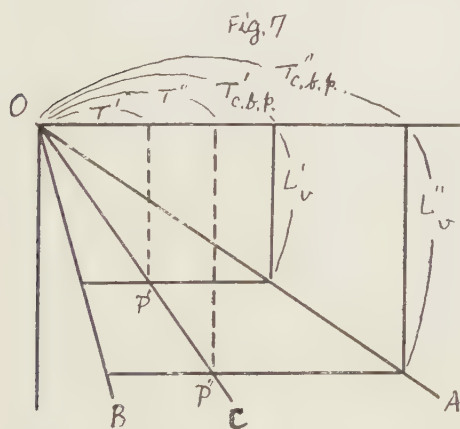


L_v , T_b , T_m and T_2 for many elements, by taking the corresponding boiling points as the reference points and by arranging them on a straight line. In Figs. 5 and 6, the latent heat of vaporization is taken as ordinate and the temperature as abscissa, and the corresponding boiling points occupy the intersections of the line OA with the vertical lines (which we shall call "the lines of heat of vaporization") whose lengths are taken to represent respectively the values of the latent heat of vaporization of the elements. Fig. 6 is drawn in enlarged scale for the rare gases entirely in the same manner as Fig. 5. In these figures the T_2 point, the melting point and the normal boiling point of the element are marked respectively by a small circle, a cross and a dot on the horizontal line passing through the position of the corresponding boiling point of that element on the line OA. Such a horizontal line representing the temperature of a substance will be called "the temperature line" of that element.

If we take the corresponding boiling points of different substances

as above the correspondency of different elements as regard to their vapour pressures can be seen very clearly with Figs. 5 and 6. If we call p/p_0 "the relative vapour pressure" for the sake of convenience then the relative vapour pressure is constant for all elements at their corresponding boiling points which lie on the straight line OA. Moreover, we can see easily with Figs. 5 and 6

that the relative vapour pressures of different elements at the temperatures determined by the intersections of their temperature lines with a straight line passing through the origin are the same for all substances. In order to illustrate this point, an outline of Figs. 5 and 6 are represented by Fig. 7, where the line OA, vertical and horizontal lines etc. have the same significances as in the case of Figs. 5 and 6. Let the latent heats of vaporization of two different substances be L_v' and L_v'' , and their corresponding boiling points be $T'_{c.b.p.}$ and $T''_{c.b.p.}$ respectively. Next let OC be a straight line passing through the origin O, the points P' and P'' be the points of intersection of the line OC with the temperature lines of two different substances



respectively, and T' and T'' be the temperatures corresponding to the points P' , and P'' respectively. Then we have

$$\frac{T'}{T''} = \frac{L_v'}{L_v''} = \frac{T'_{c.b.p.}}{T''_{c.b.p.}}, \dots\dots\dots(5)$$

and consequently

$$\frac{L_v'}{T'} = \frac{L_v''}{T''} \dots\dots\dots(6)$$

This makes the relative vapour pressures of two different substances the same at the temperatures T' and T'' respectively. Thus the temperatures determined by the positions on a straight line passing through the origin can be considered to be the corresponding temperatures for different substances; and the liquid state of different substances at their corresponding temperatures can be regarded as the corresponding state, so far as the vapour pressure is concerned. If the straight line OC moves from left to right by keeping the position of O fixed, then the relative vapour pressure, which is the same for different substances at the corresponding temperatures determined by the position of OC, increases. On the contrary, if the line OC moves from right to left the relative vapour pressure decreases.

Next, the T_2 points of different substances must be investigated in connection with the corresponding temperature. For this purpose let us imagine that the substances are in super-cooled state below their melting points. Now we shall consider the case, in which the T_2 points of two different substances lie on a same straight line which passes through the origin. Let the points P' P'' in Fig. 7, whose temperatures are respectively T_2' and T_2'' , be such two T_2 points of different substances, then we have from equation (5)

$$\frac{T_2'}{T_2''} = \frac{L_v'}{L_v''} = \frac{T'_{c.b.p.}}{T''_{c.b.p.}} \dots\dots\dots(6)$$

If we represent the latent heats of fusion of the two substances by L_f' and L_f'' respectively, we get from equation (1)

$$T_2' = \frac{L_f'}{2R} \text{ and } T_2'' = \frac{L_f''}{2R}$$

for all the monoatomic elements. By using these values of T_2' and T_2'' (6) becomes

$$\frac{L_f'}{L_f''} = \frac{L_v'}{L_v''};$$

and consequently we get

$$\frac{L_f'}{L_v'} = \frac{L_f''}{L_v''} \dots\dots\dots(7)$$

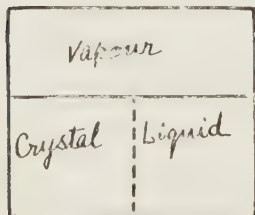
This shows that for different substances whose T_2 points lie on a same straight line passing through the origin the ratio of the two latent heats, of fusion and of vaporization, is constant. It is also evident that the T_2 points of different substances whose values of L_f/L_v are different do not lie on a same straight line passing through the origin. As is seen in Fig. 5, the positions of the T_2 points for different substances are scattered to some extent; but, roughly speaking, they may be considered to be crowded near the straight line OB which passes through the origin. This indicates that the value of L_f/L_v does not much differ according to the kind of substances. The values of L_f/L_v for the elements are given in the 5th column of Table II. The values for rare gases are comparatively great, but for the other substances they are not much different from each other. By taking an average for all the elements tabulated in Table II the value of 0.0318 was obtained as the mean, and the straight line OB in Figs. 5 and 6 was drawn with this mean value. From these figures the relative situation of the T_2 points i.e. the values of L_f/L_v for different substances can be seen very clearly. When the T_2 point of a substance is situated to the right of the line OB the value of L_f/L_v is greater than the mean value, and when it is situated to the left the value of L_f/L_v is smaller than the mean value. Thus Figs. 5 and 6 show very clearly the correspondency or uncorrespondency of different elements with regard to their values of L_f/L_v as well as their relative vapour pressures. As is stated above, the T_2 points of the elements are rather crowded in the vicinity of the line OB. This is not the case with their melting points, whose positions in Fig. 5 are much scattered indicating that the correspondency of the melting points of different elements is much worse than that of the T_2 points. This shows that the difference of the relative vapour pressure with the kind of substances is much greater at the melting point than at the T_2 point.

The positions, in Figs. 5 and 6, of the normal boiling point and melting point of arsenic, and of the T_2 points and the melting points of rare gases are different from those of other elements. For the latent heat of vaporization of liquid arsenic the writer assigned approximately the same value as that of its solid. But the abnormality of arsenic as stated above is not due to this approximation. It is entirely caused by an enormously high vapour pressure for the solid state, so that its melting takes place at the temperature higher than the boiling point and under enormously high vapour pressure. With

rare gases all of the T_2 points, the melting points and the normal boiling points appear to the right of the corresponding boiling point line OA. This is due to the facts that their melting points are very close to their normal boiling points and also that their latent heats of vaporization are much smaller than the average thus causing their corresponding boiling points to become much lower. However such abnormality with rare gases will entirely disappear if we turn the corresponding boiling point line OA to the right.

The T_2 points of the elements are proportional in general to their latent heats of fusion. But the melting points have no such direct concern with the latent heats of fusion as is evident from Fig. 10 of the former paper; and the reason for this will be now considered. As is stated above the vapour pressure at the melting point has a direct connection with the value of T_b/T_m or $T_{c.b.p.}/T_m$, and the former increases as the melting point approaches to the normal or corresponding boiling point. Considered from this view point, it will be fruitful to interpret the melting point by means of the magnitude of the vapour pressure at that point. To do this, it is more convenient to consider on the triple point instead of on the melting point, as the latter is practically the same as the former. Let us suppose that the vapour, the liquid and the crystal phases of a substance are in equilibrium in a closed vessel as is shown in Fig. 8, and that the manner of energy levels for a molecule in these three states is as shown

Fig. 8



in Fig. 9. In this figure L_v and L_f are the latent heats of vaporization and of fusion respectively, and N is Loschmidt's number. Thus L_v/N and L_f/N represent respectively the energies which are necessary to carry one molecule from liquid to vapour and from crystal to liquid. Now let us assume that in the transition of a molecule from crystal to liquid some more energy P is necessary in excess of L_f/N . This excess potential energy, which will be called "the excess potential barrier", is represented by a broken line in Fig. 9; and it is to be jumped over by the molecules in their transition from crystal to liquid or vice versa. The presence of such excess

Fig. 9

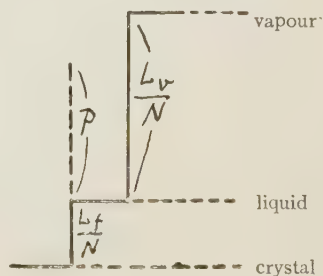
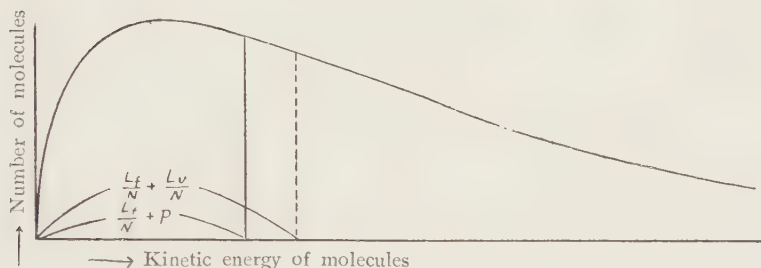
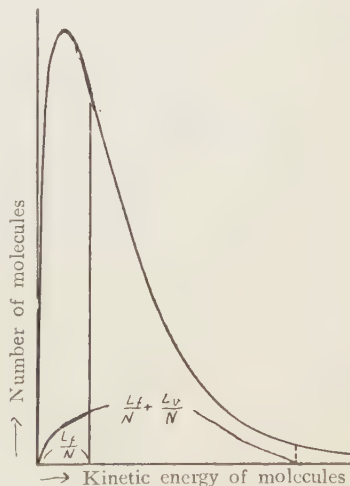


Fig. 10



potential barrier, which does not appear in the thermodynamical treatment, will hinder the molecules from travelling mutually between the crystal and the liquid phases, and will affect the melting point of the crystal and consequently the vapour pressure at that point. The effect of the presence of the excess potential barrier seems to be understood more clearly by considering the distribution of the kinetic energy among the molecules in the crystal. The curves shown in Figs. 10 and 11 represent diagrammatically such distribution of the kinetic energy among molecules by taking the number of molecules as ordinate and the magnitude of the kinetic energy as abscissa, and they correspond to two different temperatures, being much higher in Fig.

Fig. 11



10. Now let us compare two extreme cases: (1) when the excess potential barrier P is very great, and (2) when P is zero. In the first case the height of the potential level $\frac{L_f}{N} + P$ which the crystal molecules must jump over in going to the liquid is not much different from the potential height $\frac{L_f}{N} + \frac{L_v}{N}$ which the crystal molecules must jump over in subliming to the vapour. In Fig. 10 these two potential heights are represented by the full and the broken lines respectively. As these two lines are situated very closely the number of molecules possessing the kinetic energy greater than that just necessary in melting and in subliming will not be much different. Consequently if the temperature about this state is that of the triple point, we can see

that the vapour pressure at the triple point or the melting point is considerable, because the number of subliming molecules is considerable, being the same as that of molecules condensing from the vapour to the crystal in equilibrium. Next, let us consider the second case where P is zero. In this case the height of the potential level $\frac{L_f}{N}$ which the crystal molecules must jump over in melting is very much smaller than $\frac{L_f}{N} + \frac{L_v}{N}$ which the crystal molecules must jump over in subliming to the vapour. Thus is obtained a considerable number of molecules which can transform into the liquid from the crystal, as is seen in Fig. 11, at a temperature much lower than that in the case of Fig. 10. This shows that the melting point is very much lowered when compared with the case of Fig. 10. If we take the potential height for the sublimation in this case as the same as in the case of Fig. 10, the number of molecules which sublime into the vapour is reduced remarkably due to the decrease of temperature of equilibrium, as is seen in Fig. 11. This shows that the vapour pressure at the triple point or at the melting point is reduced remarkably. The two cases considered above are the extreme ones; and the heights of the excess potential barrier for many elements will be within these two extremes. Consequently the degree of the effect of the presence of the excess potential barrier upon the increase of the melting point and of the vapour pressure at the melting point will be different from element to element, being greater with higher excess potential barrier.

The above argument is entirely qualitative. However, the general tendency of the vapour pressure at the melting points of the elements,— that it increases as the melting point approaches to the boiling point and at the same time as the melting point recedes apart from the T_2 point as was seen from Figs, 2, 3, 4, 5 and 6, — will be clearly understood in the above way. Moreover, the above view assuming the presence of the excess potential barrier in the transition from crystal to liquid or vice versa affords a very probable explanation for why the melting point of a substance does not directly depend upon its latent heat of fusion.

As the height of the excess potential barrier diminishes the melting point recedes apart from the boiling point, and approaches to the T_2 point which is determined by the latent heat of fusion. With the rare gases the melting points are very close to their respective T_2 points as is seen in Fig. 1, and the height of the excess potential barriers

is likely to be very small as compared with their latent heat of fusion. However the ratios of L_f/L_v are exceptionally great in these cases, and consequently the values of $\left(\frac{L_f}{N} + P\right) / \left(\frac{L_f}{N} + \frac{L_v}{N}\right)$ which affect the vapour pressure remains remarkably great despite of the small value of P . This acts entirely in the same way as when P is very great, and causes the enormous vapour pressure at the triple point or the melting point by bringing the boiling point also very close to the melting point. With arsenic, whose value of the latent heat of fusion is not known, we can not enter into details in this connection, though an enormous vapour pressure of 36 atmospheres at its triple point seems to be due to its exceptionally large value of

$$\left(\frac{L_f}{N} + P\right) / \left(\frac{L_f}{N} + \frac{L_v}{N}\right).$$

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Sur l'Existence de Solutions pour une Équation différentielle ordinaire

par **Hiroshi Okamura**

(Reçu le 7 Novembre, 1941)

Nous avons établi récemment une condition nécessaire et suffisante pour qu'un système normal d'équations différentielles ordinaires avec seconds membres continus n'admette qu'une solution unique à droite d'un point initial, pris arbitrairement dans un voisinage d'un point intérieur du domaine de définition.¹ Pour le cas d'une équation différentielle

$$(1) \quad \frac{dy}{dx} = F(x, y)$$

avec une fonction F continue dans un domaine D de points (x, y) , la condition exprime l'existence d'une fonction $\Phi(x, y, z)$, qui est continue, ainsi que ses dérivées partielles du premier ordre, dans un domaine formé de tous points (x, y, z) correspondant à deux points (x, y) et (x, z) contenus dans un voisinage d'un point considéré de D , et telle que

$$(2) \quad \Phi(x, y, z) > 0 \text{ ou } = 0 \text{ selon que } |y - z| > 0 \text{ ou } = 0$$

et

$$(3) \quad \frac{\partial \Phi(x, y, z)}{\partial x} + \frac{\partial \Phi(x, y, z)}{\partial y} F(x, y) + \frac{\partial \Phi(x, y, z)}{\partial z} F(x, z) \leq 0.$$

Dans le présent mémoire, nous supposons que cette condition soit réalisée d'avance et nous donnerons une généralisation de la méthode de Cauchy-Lipschitz pour démontrer l'existence d'une solution dans ce cas. On sait, en réalité, la dite existence, d'après Peano, néanmoins nos raisonnements sont très simples et c'est une généralisation ultime dans un certain sens, parce que, si l'on se place dans des circonstances plus étendues, on ne peut plus assurer l'unicité des solutions. En outre, la conception utilisée dans cette méthode nous permet de démontrer l'existence d'une ou plusieurs solutions en un point singulier, ou des solutions asymptotiques, d'une équation différentielle, ce que nous exposerons aussi dans la suite.

1. Okamura, ces *Memoirs A* **24** (1942), p. 21.

Il est à remarquer que des résultats analogues subsisteront pour un système différentiel de plusieurs équations simultanées.

I.—Méthode de Cauchy-Lipschitz.

Supposons, pour fixer les idées, que, dans l'équation (1), $F(x, y)$ soit une fonction continue dans un rectangle fermé

$$R: 0 \leq x \leq a, |y| \leq b,$$

avec $a \leq \frac{b}{M}$ ($a, b, M > 0$), tel que $|F(x, y)| \leq M$ dans R , et que l'on ait une fonction $\Phi(x, y, z)$, continue, ainsi que ses dérivées partielles du premier ordre, pour $0 \leq x \leq a, |y| \leq b, |z| \leq b$ et satisfaisant aux conditions (2) et (3) dans la même région des variables (x, y, z) .

Alors, pour établir la solution de (1) issue à droite de l'origine $(0, 0)$, la méthode de Cauchy-Lipschitz consiste à former, comme solution approximative, une ligne polygonale issue de l'origine, telle que, dans son équation

$$y = \varphi(x) \quad [0 \leq x \leq a, \varphi(0) = 0]$$

on ait

$$|\varphi'(x) - F[x, \varphi(x)]| < \varepsilon$$

pour $0 \leq x \leq a$ (sauf, bien entendu, un nombre fini de points x correspondant à des points anguleux de la ligne polygonale) avec la borne d'erreur $\varepsilon (> 0)$ arbitrairement assignée, ce qui est possible, évidemment, d'une infinité de manières, et puis à démontrer la convergence de cette fonction vers une solution $y(x)$ de (1) avec le décroissement indéfini de ε , au moyen de la condition de Lipschitz imposée à la fonction $F(x, y)$. Mais cette dernière condition n'est nullement nécessaire, et on peut démontrer la convergence de $\varphi(x)$, par l'hypothèse de l'existence de Φ faite tout à l'heure, comme il suit.

Soient, en effet, $\varphi(x)$ et $\psi(x)$ deux telles solutions approximatives avec la même borne d'erreur ε comme ci-dessus. Alors on a

$$\Phi[0, \varphi(0), \psi(0)] = \Phi(0, 0, 0) = 0 \quad [\text{par (2)}]$$

et

$$\begin{aligned} \Phi[x, \varphi(x), \psi(x)] &= \int_0^x \frac{d}{dx} \Phi[x, \varphi(x), \psi(x)] dx \\ &= \int_0^x \left[\frac{\partial \Phi}{\partial x} + \frac{\partial \Phi}{\partial y} \varphi'(x) + \frac{\partial \Phi}{\partial z} \psi'(x) \right]_{\substack{y=\varphi(x) \\ z=\psi(x)}} dx \\ &\leq \int_0^x \left\{ \frac{\partial \Phi}{\partial y} [\varphi'(x) - F(x, y)] + \frac{\partial \Phi}{\partial z} [\psi'(x) - F(x, z)] \right\} dx \\ &\quad [\text{par (3)}] \end{aligned}$$

$$\begin{aligned} &\leq \int_0^x \left(\left| \frac{\partial \Phi}{\partial y} \right| + \left| \frac{\partial \Phi}{\partial z} \right| \right) \varepsilon dx \\ &\leq 2K\varepsilon x \leq 2K\varepsilon a \end{aligned}$$

en supposant que $\left| \frac{\partial \Phi}{\partial y} \right| < K$, $\left| \frac{\partial \Phi}{\partial z} \right| < K$ dans R . La dernière quantité $2K\varepsilon a$ tend vers zéro avec ε , donc d'après la condition (2) et la continuité de Φ , on a

$$|\varphi(x) - \psi(x)| < \eta \quad (0 \leq x \leq a)$$

avec une borne η dépendant seulement de ε et infiniment petite en même temps que ε . Ce résultat suffit à conclure la convergence uniforme de $\varphi(x)$ dans l'intervalle $0 \leq x \leq a$ vers une fonction $y(x)$ pour $\varepsilon \rightarrow 0$ et $y(x)$ est la solution voulue parce que, comme limite pour $\varepsilon \rightarrow 0$ de l'inégalité

$$\left| \varphi(x) - \int_0^x F[x, \varphi(x)] dx \right| \leq \varepsilon x,$$

on a

$$y(x) = \int_0^x F[x, y(x)] dx.$$

La solution issue à droite de l'origine (0, 0) est unique et notre condition contient, comme cas particulier, celle de Lipschitz, ce que nous avons indiqué à plusieurs reprises (loc. cit.).

II.—Existence de solutions asymptotiques.

En vue d'applications ou d'extensions naturelles des idées précédentes, nous nous placerons maintenant dans les hypothèses suivantes :

Étant donnée l'équation (1), supposons que la fonction $F(x, y)$ soit continue dans un domaine V ,¹ qui renferme dans son intérieur, pour $a < x < b$ (a, b : finis ou infinis), une courbe

$$y = \psi(x) \quad (a < x < b)$$

où la fonction $\psi(x)$ soit continue, ainsi que sa dérivée $\psi'(x)$, pour $a < x < b$ et que la partie du domaine V entre deux parallèles $x = a'$, $x = b'$, soit bornée pour tout choix de a' et b' tel que $a < a' < b' < b$. Supposons ensuite qu'il existe une fonction $\Phi(x, y, z)$ de telle façon que :

1° $\Phi(x, y, z)$ soit continue dans un domaine W de points (x, y, z) correspondant à deux points (x, y) et (x, z) de V et satisfasse à la condition (2) dans W , et que ses dérivées partielles Φ'_x , Φ'_y et Φ'_z

1. Pour appliquer le résultat, on doit choisir convenablement le domaine V plus ou moins étroit (ou large) selon le but.

soient continues dans W sauf des points (x, y, z) tels que $y=z$, c'est-à-dire qu'elles sont continues dans la partie de W telle que $y \neq z$, et elles vérifient l'inégalité (3) (pour $y \neq z$, bien entendu);

2° on ait, dans W ,

$$|\Phi_z(x, y, z)| \leq L(x) \quad (a < x < b, y \neq z),$$

où la fonction $L(x)$ est telle que le produit $L(x)|\phi'(x) - F[x, \phi(x)]|$ soit sommable pour $a < x < b' < b$, c'est-à-dire

$$\int_a^{b'} L(x)|\phi'(x) - F[x, \phi(x)]| dx < \infty \quad \text{pour } a < b' < b;$$

3° la fonction $\Phi[x, y, \phi(x)]$ possède une succession de valeurs aux limites continue sur la frontière de V pour $a < x < b$, donc on peut considérer que la fonction $\Phi[x, y, \phi(x)]$ est continue dans V et sur la frontière de V pour $a < x < b$, et l'on a, pour tout point $(\bar{x}, \bar{y})$ sur la frontière de V ($a < \bar{x} < b$), l'inégalité

$$\Phi[\bar{x}, \bar{y}, \phi(\bar{x})] \geq \omega(\bar{x}) > 0$$

avec une fonction $\omega(x)$ continue et positive pour $a < x < b$.

Sous ces hypothèses, nous démontrerons les deux propositions suivantes (A et B).

A.—Si, pour un point (x_0, y_0) intérieur de V ($a < x_0 < b$), on a

$$\Phi[x_0, y_0, \phi(x_0)] + \int_{x_0}^x L(x)|\phi'(x) - F[x, \phi(x)]| dx < \omega(x)$$

pour $x_0 \leq x < b$,

alors la solution (unique) de l'équation (1) partant à droite du point (x_0, y_0) peut se prolonger jusque $x=b$, passant dans l'intérieur de V .

On sait, en effet, l'existence unique d'une telle solution au voisinage à droite du point $x=x_0$, en vertu du § I par exemple. Donc, il nous reste la possibilité du prolongement à droite jusque $x=b$. Soit $y=y(x)$ la solution de (1) située dans V pour $x_0 \leq x \leq x_1 < b$ et considérons la fonction $\Phi[x, y(x), \phi(x)]$. Alors, en désignant par ξ la plus grande des valeurs x telles que $y(x)=\phi(x)$ ($x_0 \leq x \leq x_1$) s'il en existe, sinon en posant $\xi=x_0$, nous avons

$$\begin{aligned} & \Phi[x_1, y(x_1), \phi(x_1)] - \Phi[x_0, y(x_0), \phi(x_0)] \\ & \leq \Phi[x_1, y(x_1), \phi(x_1)] - \Phi[\xi, y(\xi), \phi(\xi)] \quad [\text{par (2)}] \\ & = \int_{\xi}^{x_1} \left[\frac{\partial \Phi}{\partial x} + \frac{\partial \Phi}{\partial y} y'(x) + \frac{\partial \Phi}{\partial z} \phi'(x) \right]_{y=y(x)}^{z=\phi(x)} dx \\ & \leq \int_{\xi}^{x_1} \left\{ \frac{\partial \Phi}{\partial z} [\phi'(x) - F(x, z)] \right\} dx \quad [\text{par (3)}] \\ & \leq \int_{\xi}^{x_1} L(x)|\phi'(x) - F[x, \phi(x)]| dx \quad (\text{par 2}^\circ), \end{aligned}$$

d'où

$$\Phi[x_1, y(x_1), \phi(x_1)] \leq \Phi[x_0, y(x_0), \phi(x_0)] + \int_{x_0}^{x_1} L(x) |\phi'(x) - F[x, \phi(x)]| dx.$$

Ce second membre est une fonction continue de x_1 , inférieure, par hypothèse, à la fonction continue $\omega(x_1)$, donc d'après 3°, la courbe $y=y(x)$ ne s'approche pas de la frontière de V jusque $x=b$, c. q. f. d.

B.—Si l'on a

$$\int_a^x L(x) |\phi'(x) - F[x, \phi(x)]| dx < \omega(x) \quad \text{pour } a < x < b,$$

alors il existe une courbe solution de (1), $y=Y(x)$ ($a < x < b$), située dans V , et $y=Y(x)$ est la seule solution de (1) telle que la courbe $y=Y(x)$ est située dans V pour x suffisamment voisin de a et telle que

$$\lim_{x \rightarrow a} \Phi[x, Y(x), \phi(x)] = 0.$$

À cet effet, désignons par $y=y_a(x)$ une solution de (1) issue à droite du point $(a, \phi(a))$, qui se prolonge jusque $x=b$ d'après A. Alors, la fonction $y_a(x)$ tend, pour $a \rightarrow a$, uniformément dans l'intervalle $a' \leq x \leq b'$ ($a < a' < b' < b$) vers une fonction (qui est nécessairement une solution de (1)), parce que, si nous prenons deux nombres a et a' tels que $a < a' < a'$, nous avons, comme dans la démonstration de A,

$$\Phi[a', y_a(a'), \phi(a')] \leq \Phi[a, y_a(a), \phi(a)] + \int_a^{a'} L(x) |\phi'(x) - F[x, \phi(x)]| dx,$$

où

$$\Phi[a, y_a(a), \phi(a)] = \Phi[a, \phi(a), \phi(a)] = 0 \quad [\text{par (2)}],$$

et l'on a par (3), comme dans A, pour $a' \leq x < b$,

$$\begin{aligned} \Phi[x, y_a(x), y_a(x)] &\leq \Phi[a', y_a(a'), y_a(a')] \\ &= \Phi[a', y_a(a'), \phi(a')], \end{aligned}$$

donc

$$\Phi[x, y_a(x), y_a(x)] \leq \int_a^{a'} L(x) |\phi'(x) - F[x, \phi(x)]| dx,$$

cette quantité étant infiniment petite pour $a \rightarrow a$, $a' \rightarrow a$, grâce à 2°. Il s'ensuit de là, d'après (2) et la continuité de Φ , la convergence de $y_a(x)$. Posons

$$Y(x) = \lim_{a \rightarrow a} y_a(x).$$

Alors la courbe $y=Y(x)$ se trouve dans l'intérieur de V parce que, comme limite pour $a \rightarrow a$ de l'inégalité facile [par (3) et 2°]

$$\Phi[x, y_a(x), \phi'(x)] \leq \int_a^x L(x) |\phi'(x) - F[x, \phi(x)]| dx \quad (a < x < b),$$

on a

$$\Phi[x, Y(x), \psi(x)] \leq \int_a^x L(x) |\psi'(x) - F[x, \psi(x)]| dx,$$

qui est $< \omega(x)$ d'après hypothèse. Par conséquent, $y = Y(x)$ est une solution de (1) située dans V .

Inversement s'il existe une solution $y = y(x)$ de (1), située dans V pour x suffisamment voisin de a , telle que

$$\lim_{x \rightarrow a} \Phi[x, y(x), \psi(x)] = 0,$$

on a, comme précédemment,

$$\Phi[x, y(x), y_a(x)] \leq \Phi[a, y(a), \psi(a)] \quad (a < a < x)$$

et, en faisant tendre a vers a , on arrive à l'égalité

$$\Phi[x, y(x), Y(x)] = 0$$

valable au voisinage de $x = a$, qui exige que $y(x) = Y(x)$, d'après (2), c. q. f. d.

Exemple.—Nous appliquerons ces résultats à des recherches de solutions asymptotiques dans le cas particulier suivant.¹

Soit une équation différentielle

$$\frac{dy}{dx} = F(x, y)$$

où $F(x, y)$ est continue pour $-\infty < x < +\infty$, $|y| \leq c$ ($c > 0$), vérifiant l'inégalité

$$\frac{F(x, y) - F(x, z)}{y - z} \leq -k < 0 \quad (y \neq z, |y| \leq c, |z| \leq c)$$

et telle que

$$\lim_{x \rightarrow +\infty} F(x, 0) = 0, \quad \lim_{x \rightarrow -\infty} F(x, 0) = 0.$$

Sous ces hypothèses nous démontrerons qu'il y a une famille à un paramètre de solutions asymptotiques à zéro pour $x \rightarrow +\infty$ et que, d'autre part, il existe une solution asymptotique à zéro et une seule pour $x \rightarrow -\infty$.

Posons, à cet effet, dans les résultats précédents,

$$\Phi(x, y, z) = e^{kx} |y - z|, \quad \psi(x) = 0, \quad L(x) = e^{kx},$$

1. Cf. Cotton, Approximations successives et équations différentielles (Mémorial des sci. math. XXVIII) (1928), p. 36-37. Il s'agit ici des solutions asymptotiques et nous ne traiterons pas le cas d'un point singulier x fini qui revient au cas précédent (x infini) par un changement de variable, comme indique M. Cotton (loc. cit., n° 16). Mais ce second cas (x fini) a été l'objet d'un travail récent de M. Haag [Bull. Sci. math. 2^e sér. 60, (1936), p. 131], qui emploie directement la méthode d'approximations successives (comme M. Cotton), tandis que notre méthode s'y applique directement aussi. Nos résultats seront un peu différents de ceux de MM. Cotton et Haag.

en prenant le domaine V défini par

$$|y| < \chi(x), \quad 0 < \chi(x) \leq c$$

avec une fonction continue $\chi(x)$ pour $-\infty < x < +\infty$. On aura alors

$$\omega(x) = \chi(x)e^{kx}.$$

Ainsi se vérifient toutes les conditions 1°-3° ($a = -\infty$, $-\infty < b \leq +\infty$).

La condition de l'énoncé A s'exprime par l'inégalité

$$e^{kx_0}|y_0| + \int_{x_0}^x e^{kx}|F(x, 0)|dx < \chi(x)e^{kx} \text{ pour } x_0 \leq x < +\infty,$$

qui est réalisée pour x_0 suffisamment grand tel que

$$|F(x, 0)| < kc \text{ pour } x_0 \leq x < +\infty$$

et pour $|y_0|$ suffisamment petit, avec une fonction convenable $\chi(x)$ telle que $\lim_{x \rightarrow +\infty} \chi(x) = 0$, parce que nous avons évidemment

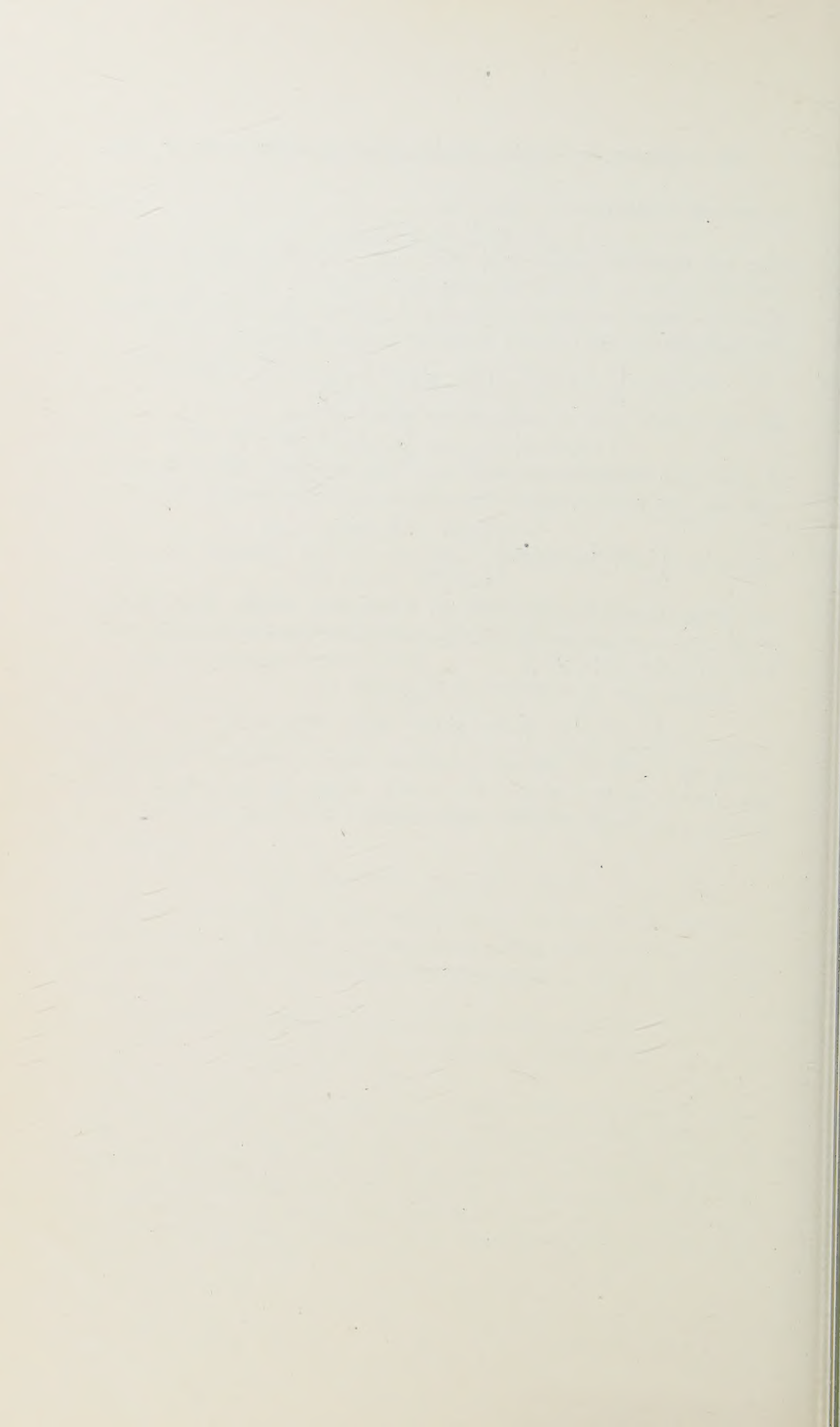
$$\int_{x_0}^x e^{kx}|F(x, 0)|dx \begin{cases} < ce^{kx} & (x_0 \leq x < +\infty), \\ = o(e^{kx}) & (x \rightarrow +\infty). \end{cases}$$

Donc, d'après la proposition A, il y a une famille de solutions $y = y(x, y_0)$ à un paramètre y_0 [$y(x_0, y_0) = y_0$] asymptotiques à zéro pour $x \rightarrow +\infty$ [$|y(x, y_0)| < \chi(x)$].

D'autre part, la condition de B revient à

$$\int_{-\infty}^x e^{kx}|F(x, 0)|dx < \chi(x)e^{kx} \text{ pour } -\infty < x < b,$$

ce qui est réalisé en prenant convenablement le nombre b et en posant $\chi(x) = c$ ou bien $\chi(x) \rightarrow 0$ ($x \rightarrow -\infty$). Donc, en vertu du résultat B, il y a une seule solution asymptotique à zéro pour $x \rightarrow -\infty$.



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